SECOND-ORDER, FULL-COULOMB ELECTRON BROADENING CALCULATIONS FOR MULTI-ELECTRON RADIATORS IN HOT, DENSE PLASMAS: A FOCUS ON DENSE PLASMA LINE SHIFTS

By

GWYNETH CLAIRE ANN JUNKEL-VIVES

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Soli Deo Gloria

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Abstract of Dissertation Presented to the Graduate School
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SECOND-ORDER, FULL-COULOMB ELECTRON BROADENING CALCULATIONS FOR MULTI-ELECTRON RADIATORS IN HOT, DENSE PLASMAS: A FOCUS ON DENSE PLASMA LINE SHIFTS

By

Gwyneth Claire Ann Junkel-Vives

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This work presents a full-Coulomb, multi-electron formalism of line broadening due to perturbation by plasma electrons. This work is based on the relaxation theory of Smith and Hooper, which was extended to treat highly ionized radiators by Tighe and Hooper. A further extension by Woltz and Hooper introduced a full-Coulomb expression of the perturber-radiator interaction in the electron broadening operator, rather than applying the dipole approximation. The term of the electron broadening operator, first order in the radiator-perturbing electron interaction is reintroduced, causing a red line shift and asymmetries. This formalism is also generalized to treat multi-electron radiating ions, using the formalism to calculate general transition arrays presented by Cowan. The effects of the plasma ions are treated dynamically using an ion microfield probability distribution with the model introduced by Boercker, Iglesias, and Dufty.

The line shapes calculated using this model are dramatically shifted and distorted with respect to lineshapes calculated in the dipole approximation of the radiator-perturbing electron interaction. They also are narrower and the differences between the two models increase as the principal quantum number of the upper state of the transition increases. This can be attributed to the fact that the orbital size is greater relative to the average plasma electron spacing. The asymmetries are attributed to the dependence of the level shifts on angular momentum state. There is good agreement between the shift calculations compared with those of Griem *et al.* and Nguyen *et al.* The line profiles are also compared to those calculated using a semi-classical model that is carried to all orders in the radiator-perturbing electron interaction. Analysis of K-shell Ar spectra using the shifted line spectra is shown. Finally, the impact of the line shift on merging of adjacent lines in a Rydberg series at ultra-high densities, $< 3 \times 10^{24} \mathrm{cm}^{-3}$, is considered.

CHAPTER 1
INTRODUCTION

1.1 Plasma Line Broadening: A Brief Survey

The study of plasma line broadening has been employed for years to characterize hot, dense plasmas [1, 2]. As a radiator interacts with a plasma, the energy levels of its bound states are modified by interactions with the surrounding ions and electrons, resulting in broadened line spectra that is dependent on the plasma density and temperature. Since the 1970's, high-powered lasers have been used to implode gas-filled micro-balloons [3]. Usually the gas fill consists of deuterium and/or tritium doped with trace amounts of elements with greater nuclear charge Z. As technology improved, progressively larger and more powerful lasers have become available, and this has led to the creation of plasmas with ever increasing densities and temperatures [4, 5, 6, 7].

The understanding of these plasmas has necessitated continuing advances in theoretical plasma line broadening, beginning with Stark broadening of neutral radiators due to the ion microfield as well as broadening due to plasma electrons [8, 9]. The line broadening formalism was extended for ionic radiators when temperatures and densities become too high to study spectra from neutral radiators [10, 11, 12], as well as full-Coulomb calculations when the dipole approximation was no longer valid, again at high densities [13, 14]. Then, with the availability of the Nova- and 24-beam Omega lasers, it was possible not only to see K-shell Ar lines but the

satellites of the resonance lines as well. At the same time it was possible to observe broadened L-shell lines from krypton. This was propitious since we had the theoretical capability to calculate the spectra from multi-electron radiators with the computer code MERL [15, 16]. Multi-electron calculations could treat L-shell lines [17] and also lines from several ionization stages [5, 6, 18].

As plasma electron densities on the order of $1 \times 10^{24}\text{cm}^{-3}$ were reached, the controversial Plasma Polarization Shift was unambiguously observed and diagnosed [19, 20, 21, 22]. The radiators were so highly ionized and the plasma electron densities were so great that the electrons penetrating radiator orbitals could shield the nucleus from the radiator electron, thus lowering its energy state. Although spectral line broadening due to plasma ions and electrons has been observed for many years and has been shown to be consistent with existing theories at lower plasma densities [23, 24], the existence of plasma-induced line shifts has only recently been widely accepted.

As early as twenty years ago [1, 25], interest in spectra of ionized radiators in dense plasmas motivated ad hoc calculations of red shifts induced by perturbing electron shielding of the nucleus. Early attempts to calculate the shift employed linearized Debye-Huckel potentials, while others used self-consistent static charge distributions to describe the shielding of the nucleus [24, 26, 27, 28, 29]. These calculations of what was called the Plasma Polarization Shift (PPS) frequently overestimated the shifts observed experimentally, particularly those using the Debye-Huckel model. This shift was often written as a first order average interaction between the radiator and the plasma electrons, and Cooper, Kelleher and Lee [30] cautioned against introducing an ad hoc shift term in conjunction with

the electron broadening operator, pointing out that a shift term should naturally arise as the real part of the broadening operator, while the imaginary part serves to broaden the line-shape. Boercker and Iglesias [31] had stated that, for neutral radiators, the first order average interaction was negligible and showed that there was significant cancelation in the terms second order in the interaction potential. This result was sometimes misinterpreted to mean that the entire shift experienced substantial cancelation. This misunderstanding and the poor agreement of early theories with the little available data led some to meet any line shift calculations with skepticism.

Ultimately, line shift calculations for highly ionized, moderate Z radiators that employed scattering theory first order in the radiator-perturbing electron interaction provided results that agreed well with each other and eventually with experiment [23, 24]. In order to obtain a consistent result for both line broadening and a line shift, Nguyen *et al.* used quantum mechanical impact theory to calculate shift and width terms for Lyman series members of high-Z radiators $\gtrsim 10$ [24]. The calculation of Nguyen *et al.* included all terms of the multipole expansion of the radiator-perturbing electron interaction, up to the octopole. These researchers discovered that the monopole term of the interaction in which the plasma electron penetrates the radiator orbital contributed the most to the shift. This is significant because the electron broadening operator was usually calculated in the dipole approximation, which, although valid for higher order terms, allowed the first order shift term to reduce to zero erroneously. Griem *et al.* [23] applied a distorted wave scattering approach to the problem, employing perturber wavefunctions distorted by only the monopole term of the radiator-perturbing electron interaction. This

first-order impact calculation summed the phase shifts of the partial waves to obtain the line shifts for He-like Ar. The results were in good agreement (within $\lesssim 10\%$) with Nguyen *et al.* [24] and the calculation demonstrated that the bulk of the shift could be obtained by including only the monopole term of the radiator-perturbing electron interaction potential.

However, when researchers attempted to present shift measurements, many objections were raised. Only recently has a consensus been reached as line shift observations confirmed the calculations by Nguyen *et al.* [24] and Griem *et al* [23]. One obstacle to an early experimental verification of shifts of spectra emitted from highly charged radiators was the attention paid to K-shell α-lines, because we now know α-lines experience very small shifts relative to higher lying series members and which were also most likely to be obscured by opacity effects. In the following paragraphs we will outline two important experiments where shifts were observed and the concerns that were raised.

Hammel *et al.*, [5] measured a red shift in the He-β line of Ar, approximately 11eV at an electron density of approximately 1.2×10^{24} cm^{-3}, which was roughly consistent with the theories of Nguyen *et al.* and Griem *et al.* and was greater than the instrumental width of their high-resolution spectrometer. However, the presence of dielectronic satellites on the red wing complicated the shift measurement and obscured asymmetries arising from the differing shifts of the various angular momentum states.

Leng *et al.*, [32] observed small red shifts and a marked asymmetry of the Ly-γ of CVI. The bulk shifts of the lines seemed to be comparable with those calculated by Nguyen, However, the theoretical line-shapes were calculated using an

average shift, as opposed to incorporating shifts dependent on the angular momentum states of the radiator into the initial line-shape calculation. Therefore, Leng *et al.* employed theoretical line-shapes that neglected the asymmetries due to these differing shifts. In addition, existing plasma density gradients could have obscured details associated with line shifts, particularly shift asymmetries. Further objections arose because the lines for different densities were convolved together to compensate for plasma gradients, which would have interfered further with a definitive shift measurement. Finally, relying heavily on the correctness of computer modeling results for the density inferences from the widths of the lines cast doubt on the application of any particular shift theory.

In the past few years, more evidence of plasma-induced line shifts has begun to appear. First, Renner *et al.* observed the Lyman series lines of aluminum shift to the red during high resolution flat target experiments [19]. In this case, the density inferences from the widths of the lines relied heavily on the correctness of computer modeling results and cast doubt on the application of any particular shift theory. Second, at Lawrence Livermore National Laboratory and the Laboratory for Laser Energetics, in implosion experiments conducted on deuterium filled microballoons, doped with trace amounts of argon, an apparent red shift of the He-β and He-γ/Lyman-β complex of K-shell Ar was observed, even after satellites were included.[18] Since some of these shifts were far in excess of the experimental error, the University of Florida group incorporated a first-order shift calculation for highly ionized radiators into our line-shape code, MERL [20]. Line shifts due to plasma electron interactions with a radiator had not been incorporated into multi-electron line-shape codes such as MERL since the existence of line-shifts had not

been conclusively observed in experiments. More recently, Woolsey *et al.* and Saemann *et al.*, reported red shifts in the He-β of K-shell argon and aluminum, respectively, both roughly consistent with Nguyen's results. [21, 22]

1.2 The Focus of this Work

We will extend the theoretical foundation of plasma line broadening by presenting a generalized full-Coulomb formalism of line broadening for multi-electron ions, where the line shifts arise consistently from the relaxation theory.

There are several reasons to study the dense plasma line shift, despite the controversy. First, since accurate plasma diagnostics has been the primary goal of plasma line broadening, it is significant if we can provide more accurate descriptions of analyzed spectra. Secondly, we will have a more complete understanding of plasma-induced modifications of energy level structure of atoms and ions. This is not a purely academic pursuit: indeed, obtaining a complete model of the plasma-induced shift provides a basis from which to understand the effect of the shift on plasma phenomenon including continuum lowering and ionization balance [33, 34, 35, 36, 37], which in turn impact opacities and line-ratio diagnostics.

Despite the success of Griem *et al.* [23] and Nguyen *et al.* [24] improvements on their work were possible. Neither presented a dynamic, in other words frequency-dependent, shift and width operator. Also, both calculations were effectively limited to first order expressions of the the radiator-perturber electron interaction. No attempt was made by Nguyen *et al.* to calculate line-shapes from the results. Finally, their work was limited to K-shell radiators. Multi-electron models are necessary for spectral-line analysis, since composite lines, that is, resonance lines

together with their accompanying satellites, are an effective diagnostic of temperature as well as electron density.

This formalism extends their work by enabling one to calculate the shift and width terms simultaneously and self-consistently using the relaxation model [9, 38]. The full-Coulomb expression of the radiator-perturbing electron interaction is necessary not only because the dipole approximation of the radiator-perturbing electron interaction breaks down at the high densities of interest, but also because the shift is dominated by the monopole term of the multipole expansion of this interaction, which is lost if only the dipole approximation is employed. Finally, this work generalizes the shift and width operator to treat arbitrary multi-electron radiators in order to address composite line spectra as well as L-shell line spectra.

1.3 Outline

In Chapter II, a theoretical basis for spectral line broadening will be presented. A set of assumptions will be put forth that are appropriate for the plasma conditions under consideration. This will allow an application of kinetic theory techniques to obtain a form of the electron shift and width operator, as described by Hussey, in order to describe the effects of the plasma electrons on the lineshape.

Chapter III will focus on the electron shift and width operator. We will introduce a useful form of the radiator-perturbing electron interaction for multi-electron ions. We will then justify the application of the second order approximation, and a generalization for multi-electron radiators will be presented. Finally, we will obtain calculable forms of the electron shift and width operator by addressing the

issue of calculating matrix elements of the interaction for complex configurations which experience intermediate angular-momentum coupling.

We will present our results in Chapter IV. The behavior of the shift as a function of various parameters will be explored, as will the impact of the level shift on line shape and position. The shifts obtained from this formalism will be compared to the theories of Nguyen and Griem, and lineshapes calculated using the current formalism will be compared to lineshapes generated from a semi-classical formalism that includes all orders in the radiator-perturbing electron interaction. Multi-electron line profiles will be shown, comparing the full-Coulomb calculation with some simpler models. Experimental data will be fit with theoretical spectra with and without the dense plasma line shift. The effect of the level shift on the phenomenon of line merging will also be demonstrated.

In the Conclusion, we will summarize our findings and consider the effects of including the dense plasma line shift on other aspects of the field of dense plasma physics.

CHAPTER 2
PLASMA LINE BROADENING

In this chapter, we will outline the theory of plasma line broadening. This work is based on a dynamical model of ion broadening and a relaxation model of electron shifts and broadening. We will first discuss the sources of line broadening with shifts in dense plasmas. Then, we will consider the time scales over which interactions between the radiator and the plasma take place in order to determine the appropriate manner in which the plasma effects should be addressed. Useful scaling parameters will also be introduced. Finally, we present the line broadening formalism including Doppler broadening due to radiator motion, a model of electron shifts and broadening using kinetic theory techniques [38, 39], and a dynamical model of ion broadening [1, 18, 40].

2.1 Model of the Plasma

In order to gain a complete understanding of all the interactions that a highly ionized radiator experiences in a plasma and how these interactions might affect line spectra emitted from such radiators, we need to develop a model of the plasma. As we indicated in the introduction, high-powered lasers have been used to implode microballoons filled primarily with deuterium and/or tritium doped with trace amounts of elements with greater nuclear charge Z. The experiments under consideration involve trace amounts of argon or krypton in deuterium or plasmas

of pure Ar or Kr, or mixtures of the two. At electron densities from 1×10^{23}/cc to better than 1×10^{24}/cc and temperatures of approximately 1 keV or greater, line spectra from K-shell Ar and L-shell Kr can be expected. At even higher temperatures, K-shell Kr has been observed [41].

At such high temperatures, the deuterium would be completely ionized. As a result, we anticipate that a radiator interacted with fast moving plasma electrons that had once been bound to the deuterium ions, as well as with the deuterium ions themselves. The deuterium ions, by virtue of their greater mass, would not be expected to have as great an average velocity as the electrons, and the Ar or Kr ions would move still more slowly. Since the gases inside the microballoons undergo spherically symmetric implosions, we can assume the bulk velocity of the plasma is zero.

As the electron density increases, we can anticipate close collisions between a radiator and plasma electrons. If the density is sufficiently high, we can expect an increasing probability of perturbing electrons penetrating the orbitals of bound radiator electrons. The nature of this interaction will necessitate a detailed understanding of individual radiator-plasma electron collisions. On the other hand, the plasma ions would be repelled as strongly as the electrons are attracted to the highly charged radiator.

Also, since the ions move more slowly than the electrons, we can anticipate that their interactions with the radiator would be screened by the plasma electrons. As a result, we will be able to treat the effects of the plasma ions collectively in terms of a fluctuating electric field due to all the plasma ions, taking into account screening due to plasma electrons.

Next, we will consider the mechanisms by which spectral lines might be altered in such a plasma.

2.2 Sources of Line Shifts and Broadening

There are several means by which spectral lines are broadened and shifted. First, there exist "natural" widths of spectral lines which can be obtained from the rates of spontaneous emission between initial and final states [1, 42]. However, for the plasma conditions under consideration, natural line broadening provides a neglible contribution to the total line width, a fraction of an electron-volt for the Ly-β of Ar^{+17}, for example.

The Doppler effect is another source of broadening and shifts. As radiators move within the plasma, the emitted photons are Doppler shifted. If there is only thermal motion, the collection of photons will be shifted both to higher and lower energies, thereby broadening the line. There can also be a line shift corresponding to bulk motion of the plasma. Doppler broadening is incorporated into the current model; however, the plasmas of interest do not experience much bulk motion and do not necessitate including a bulk-Doppler shift.

Another source of broadening arises from absorption and re-emission of photons as they travel through the plasma, *i.e.* opacity broadening. Photons are preferentially absorbed at frequencies where the intensity is the greatest, but can be re-emitted over a wide range of angles and frequencies. This has the effect of lowering the peak of a spectral line and distributing the intensity to the wings. The effects of opacity broadening will be included in the analysis of experimental

data; however this phenomenon is described in detail in other works and will not be pursued here [1, 18, 43].

We will be examining plasma regimes that are sufficiently dense that the dominant source of line broadening is due to the Stark effect. The Stark effect refers to the modification of the energy level structure of the bound radiator electrons due to an external electric field. Although both plasma electrons and ions contribute to this field, they cannot be treated in the same manner. In order to treat each type of interaction correctly, one needs to determine the time scale over which they act.

2.3 Time and Length Scales

Whether one treats the interactions of the radiator with the plasma with a quasi-static or dynamical model is dependent on the time scales over which the interactions occur, relative to the time over which the excited ion or atom radiates. A radiative lifetime corresponds to the frequency half width of a lineshape by using a relation utilizing the Uncertainty Principle, $\Delta\omega\Delta t \sim 1$. Portions of a lineshape at a large frequency separation from line center correspond to transitions occurring over a short time. If a perturber acts slowly over a time long relative to this radiative lifetime, the effect of the perturber on the radiator does not change significantly over the lifetime and may be treated using a quasi-static model. On the other hand, very small frequency separations from line center correspond to transitions occurring over a relatively long time. If the time over which a perturber acts is short relative to this radiative lifetime, the interaction between

the perturber and the radiator during the lifetime is time-dependent and the effects of the perturber must be treated dynamically.

We will now determine the change in the effect of the perturbers on the radiator for an average radiative lifetime for the plasmas under consideration. The average radiative lifetime corresponds to the experimentally observed full width at half maximum for a given lineshape. The fwhm of a K-shell β-line is approximately 40 eV, which corresponds to $\Delta t = 10^{-17}$ seconds. We will determine the relative change in the electric field of a perturber changes over this time, $\delta\mathcal{E}/\mathcal{E}$,where the electric field is defined as follows:

$$\vec{\mathcal{E}} = e\frac{\hat{\mathbf{r}}}{r^2} \tag{2.1}$$

where r is the distance between the perturber and the radiator.We now take the differential to get an expression for $\delta\mathcal{E}$,

$$\delta\mathcal{E} = e\delta(r^{-2}) = -2e\frac{\delta r}{r^3} = -2\frac{\delta r}{r}\mathcal{E}. \tag{2.2}$$

In order to set an upper bound on $\delta\mathcal{E}/\mathcal{E}$ we set δr equal to $v_{\text{ave}}\Delta t$. An average velocity of a perturbing particle of a given species can be obtained from the temperature as follows,

$$\overline{v}_j = \left(\frac{2k_B T_j}{m_j}\right)^{1/2}, \tag{2.3}$$

where k_B is the Boltzmann factor, T_j is the temperature of that species, and m_j is the mass of the species. We will consider the case of highly ionized Ar immersed

in a plasma of electrons and either deuterium or argon ions, for a temperature, $kT = 1000eV$ and an electron density of 1×10^{24}/cc.

Below, we show the values of $\delta\mathcal{E}/\mathcal{E}$ for various perturbers. We will next choose a value of r that corresponds to the distance of closest approach.

$$\begin{aligned} \left|\frac{\delta\mathcal{E}}{\mathcal{E}}\right| &< \frac{3\text{Å}}{r_c} \quad \text{for electrons} \\ &< \frac{.05\text{Å}}{r_c} \quad \text{for deuterium ions} \\ &< \frac{.012\text{Å}}{r_c} \quad \text{for argon ions} \end{aligned} \tag{2.4}$$

In order to determine the distance of closest approach for the plasma electrons, we begin with the inter-electron spacing, r_{oe},

$$r_{oe} = \left(\frac{4\pi}{3} n_e\right)^{-1/3}, \tag{2.5}$$

where n_e is the electron density. This gives us a value of .62 Å for r_{oe} at an electron density, $n_e = 10^{24}$/cc . The relative change in the electric field becomes $\delta\mathcal{E}/\mathcal{E} < 4.8$. Since the radiators under consideration are highly charged, the distance of closest approach is probably even smaller. Therefore we can assume $\delta\mathcal{E}/\mathcal{E}$ will be even larger. It is clear that we must treat the electrons dynamically.

If we consider a plasma of pure argon, we must employ the average particle distance, $r_{oi} = \overline{Z}^{1/3} r_{oe}$, where $\overline{Z}$ refers to the average charge of the perturbing ions. The value of $\overline{Z}$ will be on the order of 16 for the plasmas under consideration. This gives us a value, $\delta\mathcal{E}/\mathcal{E} < .008$, which suggests that it is appropriate to treat argon ion perturbers quasi-statically.

If the radiator is immersed in a deuterium plasma, the deuterium ions will be completely ionized and their density will roughly correspond to the electron density. As a result we get the value .08 for $\delta\mathcal{E}/\mathcal{E}$, which suggests employing a quasi-static model. However, if we consider a smaller frequency separation, for example 10 eV or less, the relative change in electric field begins to approach one. This is consistent with calculations of argon spectra employing a dynamical model of ion effects. The calculations of Ar line spectra using both quasi-static and dynamical models differed significantly only near line center [18]. Haynes *et al.* considered plasma mixtures of deuterium and argon ions and found that as the concentration of Ar ions was increased, the lineshapes calculated in the dynamic model reduced to the static limit, with little difference in the two models at approximately 20% Ar in deuterium [18].

Another appropriate time scale for the interactions of the radiator with electrons would be the time an electron can travel close to an ion and not be shielded by the intervening plasma. A length scale appropriate to the interaction would be the Debye length, λ_D, because it represents the distance past which a charge is effectively screened from the radiating ion by the plasma environment.

$$\lambda_D = \left(\frac{k_B T}{4\pi n e^2} \right)^{1/2}, \tag{2.6}$$

where n is the density of the intervening particles and e is the charge of an electron. We will attribute most of the screening to the plasma electrons.

If we determine the time it takes for an electron to travel across a Debye sphere when it has the most probable velocity for a given temperature, we obtain

a quantity that can be related to the electron plasma frequency.

$$t_e = \frac{\lambda_D}{v_e} = \left(\frac{m_e}{8\pi n e^2}\right)^{1/2} \tag{2.7}$$

$$= \frac{1}{\sqrt{2}\omega_{pe}}. \tag{2.8}$$

Therefore, the electrons must be treated dynamically when the frequency separation is less than the electron plasma frequency, which coincidentally is approximately 35 eV for an electron density, $n_e = 10^{24}/\text{cc}$. For all the spectral lines under consideration, significant portions of the line profile lie within this range.

In addition to considering the interactions of the plasma with the internal states of the radiator, we must consider the effect of the plasma on the center of mass motion of the radiator. We will be making the approximation that the velocity of the radiating ion will be constant during the lifetime of the transition: therefore, we must determine whether this approximation is valid. We can safely assume that little momentum is transfered to the radiator center of mass as it collides with plasma electrons; however, we will estimate the momentum transfered to the radiator as it interacts with the ion microfield. We will simply use the definition of impulse, assuming that the electric field can be approximated by the field due to a plasma ion at the ion sphere radius, described as follows,

$$m_r \Delta v_r = F\Delta t < \frac{Z_r Z_p e^2}{r_c^2}\Delta t, \tag{2.9}$$

where m_r, v_r, and Z_r are the mass, velocity, and charge of the radiating ion, respectively, Z_p is the charge of the perturbing ion and r_c is the distance of closest approach.

We will compare the change in momentum to the average momentum, determined using the ion temperature in the following expression:

$$\frac{m_r \Delta v_r}{m_r v_r} < \frac{Z_r Z_p e^2}{r_c^2} \frac{\Delta t}{(2 m_r k_B T)^{1/2}} \tag{2.10}$$

$$\frac{m_r \Delta v_r}{m_r v_r} < .004 \frac{Z_p a_0^2}{r_c^2}, \tag{2.11}$$

for a radiating Ar^{+17} ion at $kT = 1000$ eV. We determine this quantity for perturbing-deuterium and argon ions to be approximately .003 and .0075, respectively, for an electron density of $n_e = 10^{24}$/cc, which suggests that we can treat the center-of-mass motion independently of the other degrees of freedom of the plasma system.

There is one more quantity we will consider before we proceed with outlining the general theory. The ratio of the radiator orbital size, $\bar{r}$, to the average inter-electron spacing, r_{oe}, taken to the third power, is a measure of the average number of plasma electrons 'penetrating' an orbital at a given density. This number, α, draws attention to the need to eliminate the dipole approximation of the radiator-perturbing electron interaction at high electron densities. Also, it gives a strong indication of the likelihood that one will observe a plasma induced shift. The electron density per/cc is represented by n_e, n_q refers to the principle quantum number, l represents the orbital angular momentum, and Z_r^* is the effective charge of the radiating ion. We define α as,

$$\alpha = \left(\frac{\bar{r}}{r_{o,e}} \right)^3 = \frac{4\pi n_e a_0^3}{3} \left(\frac{3n_q^2 - l(l+1)}{2Z_r^*} \right)^3. \tag{2.12}$$

If this parameter is also applied to ions, one might draw the conclusion that a full-Coulomb representation of the radiator-perturbing ion interaction is also necessary, especially when the perturbers are deuterium ions. However, we must remember that the radiator has a positive charge and would repel the ions as strongly as the electrons are attracted. We do not need to be concerned with close interactions between the radiator and individual perturbing ions.

2.4 The Line Shape Expression

In this section, we will introduce a general power distribution for dipole radiation. We develop the expression in terms of the autocorrelation of the radiator dipole. Since the power distribution will be written in terms of an ensemble average over plasma states, we will discuss how the average will be evaluated over the various degrees of freedom within the radiator-plasma system. We will then separate out the effects of the motion of the radiator center of mass, which leads to Doppler broadening.

The power distribution of dipole radiation, as a function of frequency, ω can be written in terms of an ensemble average. The derivation of this expression has been described in many other sources and will not be presented here.[1, 2]

$$P(\omega) = \frac{4\omega^4}{3c^3} \sum_{ab} |\langle b|\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}}|a\rangle|^2 \rho_a \delta(\omega - \omega_{ab}), \tag{2.13}$$

where the radiator dipole is represented by $\mathbf{d}$, the indices a and b represent the initial and final states, respectively, of the radiator together with the plasma environment. The position of the center of mass of the radiator is denoted by $\mathbf{r}$,

and the vector, $\mathbf{k}$, represents the wavevector of the emitted radiation, ω/c. ρ_a represents the eigenvalue of the density matrix for the initial states of the radiator and the plasma environment. The energy difference of the initial and final states, $(E_a - E_b)\hbar$ is written as ω_{ab}.

The line profile can be rewritten in terms of its transform using the integral representation of a Dirac delta function,

$$
\begin{aligned}
I(\omega) &= \frac{4\omega^4}{3c^3} P(\omega) && (2.14)\\
&= \sum_{ab} \langle a|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{d}|b\rangle\langle b|\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}}\rho_a|a\rangle\delta(\omega-\omega_{ab}), && (2.15)\\
&= \frac{1}{2\pi}\sum_{ab}\int_{-\infty}^{\infty} dt\, e^{i(\omega-i\epsilon)t}\langle a|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{d}e^{iE_b t/\hbar}|b\rangle\langle b|\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-iE_a t/\hbar}\rho|a\rangle && (2.16)\\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega-i\epsilon)t}\mathrm{Tr}\{e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{d}e^{iHt/\hbar}\cdot\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-iHt/\hbar}\rho\}, && (2.17)
\end{aligned}
$$

where the trace over the plasma radiator system is denoted by $\mathrm{Tr}\{\cdots\}$.

The power distribution is now expressed in terms of in time development operators, which are derived from the usual equation of motion;

$$
i\hbar\frac{\partial}{\partial t}T(t) = HT(t) \tag{2.18}
$$

which has the solution

$$
T(t) = e^{-iHt/\hbar}, \qquad \text{where} \qquad T(0) = 1, \tag{2.19}
$$

and H is the Hamiltonian of the combined radiator and plasma system. The damping factor ϵ represents the natural line width; although it is a small factor, it serves to provide convergence for the integral in eq. 2.17 as t approaches infinity.

If we define the operator $\mathbf{d_k}(t)$ as follows,

$$\mathbf{d_k} = e^{-i\mathbf{k}\cdot\mathbf{r}}\mathbf{d} \quad \text{and} \quad e^{iHt/\hbar}\mathbf{d_k}e^{-iHt/\hbar} = \mathbf{d_k}(t), \tag{2.20}$$

we can express eq. 2.17 as the transform of the autocorrelation function of the radiator dipole, as shown below:

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega - i\epsilon)t}\mathrm{Tr}\{\mathbf{d_k}^{\dagger}\cdot\mathbf{d_k}(t)\rho\}. \tag{2.21}$$

Although this expression is interesting from a physical point of view, we need to obtain a form of the power distribution that will allow us to obtain ensemble averages over the various degrees of freedom of the radiator-plasma system. Remembering that a trace is invariant under cyclic permutations, we arrive at the following expression:

$$I(\omega) \;=\; \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega - i\epsilon)t}\mathrm{Tr}\{\mathbf{d_k}\cdot e^{-iHt/\hbar}\rho\mathbf{d_k}^{\dagger}e^{iHt/\hbar}\}. \tag{2.22}$$

Referring to eq. 2.22, we will define a Liouville operator as a commutator of an arbitrary operator with the Hamiltonian, such that

$$L\hat{f} = [H, \hat{f}] \qquad \text{and} \qquad e^{-iLt}\hat{f} = e^{-iHt/\hbar}\,\hat{f}\,e^{iHt/\hbar}, \tag{2.23}$$

in order to arrive at the following expression:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \mathrm{Tr}\{\mathbf{d_k} \cdot e^{-i(\omega - L - i\epsilon)t} \rho \mathbf{d_k}^\dagger\}. \tag{2.24}$$

Let us step back a moment and consider our ultimate goal. We currently have an expression that is an ensemble average over the entire plasma system. We wish to obtain ensemble averages over the various degrees of freedom of the radiator-plasma system. We can imagine taking the transform of the factor $e^{-i(\omega - L - i\epsilon)t}$ to get an expression of the form,

$$I(\omega) = \langle \mathbf{d_k}^\dagger R(\omega) \mathbf{d_k} \rangle, \tag{2.25}$$

where

$$R(\omega)^{-1} = \omega - L - i\epsilon. \tag{2.26}$$

We would prefer to take the average over individual plasma systems. Therefore, we will now write the full Hamiltonian of the radiator and the plasma electrons and ions,

$$H = H_r^{int} + H_r^{cm} + H_i + H_e + V_{i,e} + V_{e,r} + V_{i,r}. \tag{2.27}$$

Here, the first term refers to the internal states of the radiator while the second term refers to the center-of-mass motion of the radiator. The next two terms on the right hand side of the equation refer to the kinetic and potential energies of the respective subsystems, $H_j = T_j + V_j$. The interaction potentials between subsystems j and k are given by $V_{j,k}$. Each term of the hamiltonian corresponds

to a Liouville operator, and we can write the resolvent $R(\omega)$ as follows,

$$R(\omega)^{-1} = \omega - L_r^{int} + L_r^{cm} + L_i + L_e + L_{ie} + L_{er} + L_{ir} - i\epsilon. \tag{2.28}$$

Since the radiator dipole is not dependent on the coordinates of plasma ions and electrons, we can take an ensemble average over the plasma coordinates of the resolvent $R(\omega)$.

$$I(\omega) = \langle \mathbf{d_k}^\dagger \langle R(\omega) \rangle_{plas} \mathbf{d_k} \rangle_{rad}, \tag{2.29}$$

where the subscripts *rad* and *plas* indicate ensemble averages over the radiator and plasma degrees of freedom respectively. As a result of this average, we will obtain form of the resolvent of the form below,

$$\langle R(\omega) \rangle = 1 - \nu G(\omega)^{-1} G(\omega) \tag{2.30}$$

$$G(\omega) = \left\langle \{\omega - L_r^{int} + L_r^{cm} + L(r, \mathcal{E}) + i\nu + \langle L_{er} \rangle_e + \mathcal{M}_{er} - i\epsilon\}^{-1} \right\rangle_{\mathcal{E}} \tag{2.31}$$

where $\mathcal{E}$ represents an electric field at the location of the radiator due to the plasma ions shielded by the plasma electrons and $\langle\rangle_{\mathcal{E}}$ represents an average over a distribution of fields. The quantity $L(r, \mathcal{E})$ represents the interaction of the radiator with this ion microfield. The factor ν, along with the form of $R(\omega)$ in terms of $G(\omega)$, represents the effects due to the fluctuations of the ion microfield. The $\langle L_{er} \rangle_e$ represents mean-field effects due to the plasma electrons, the term $\mathcal{M}_{er}$ accounts for higher-order, time-varying effects or fluctuations due to the radiator interaction with the plasma electrons.

In addition to averaging over the plasma degrees of freedom, we may average over the center of mass coordinates of the radiator in order to obtain an expression for Doppler broadening. We will address this issue in the next few pages. In the following section, we will present forms of the operators listed in eq. 2.31 describing the effects of the plasma electrons and ions using certain weak coupling approximations.

We will now address the problem of radiator motion. We will treat radiator velocity as being statistically independent of the plasma environment and the internal radiator state. Another way to express this is to factor the density matrix:

$$\rho \rightarrow \rho_{cm}\rho_{r,i,e}, \tag{2.32}$$

The index, r, refers to the internal radiator states, cm refers to the the center-of-mass states, while i and e refer to the plasma ions and electrons, respectively. Although we have shown in section 2.3 that the center-of-mass motion is effectively independent of the other degrees of freedom for the plasma conditions under consideration, the reader can find quantum theories of line broadening where Stark broadening is assumed to be statistically dependent on radiator motion [44, 45, 46, 47]. For cases where the perturber mass is much less than the radiator mass it was shown that the these models reduce to the statistically independent case [45, 46].

If one assumes that the radiators behave like an ideal gas, their velocity distribution would be Maxwellian, so that

$$\rho_{cm} \equiv \left(\frac{\beta m_r}{2\pi}\right)^{3/2} e^{-\beta m_r v^2/2} = f(v). \tag{2.33}$$

The mass of the radiator is denoted by m_r and its velocity by v. We then re-express our time development operators in order to separate out the radiator's translational motion as follows:

$$e^{iHt/\hbar} \rightarrow e^{iH't/\hbar} e^{iH_{cm}t/\hbar}, \tag{2.34}$$

where H' represents the combined hamiltonian for the radiator internal states and the plasma system, and H_{cm} represents the hamiltonian for the radiator translational states. With our previous assumption, the operators on the radiator center of mass, $\mathbf{k}\cdot\mathbf{r}$, now commute with hamiltonian for the internal radiator states and the plasma system.

Since the trace in eq. 2.22 is invariant under cyclic permutations we get the following expression:

$$\begin{aligned} I(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega-i\epsilon)t} \int d\mathbf{v} f(v) \\ &\quad \mathrm{Tr}\{\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}} \cdot e^{-iH't/\hbar} e^{-iH_{cm}t/\hbar} \rho_{r,i,e} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{d} e^{iH't/\hbar} e^{iH_{cm}t/\hbar}\} \end{aligned} \tag{2.35}$$

$$\begin{aligned} I(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega-i\epsilon)t} \int dv f(v) \\ &\quad \mathrm{Tr}\{\mathbf{d}e^{-i\mathbf{k}\cdot\mathbf{r}(\mathbf{t})} \cdot e^{-iH't/\hbar} \rho_{r,i,e} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{d} e^{iH't/\hbar}\}. \end{aligned} \tag{2.36}$$

If the velocity of the center of mass is treated as constant over the lifetime of the excited state, we get the following expression:

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega-i\epsilon)t} \int dv f(v) e^{-i\mathbf{k}\cdot\mathbf{v}t} \mathrm{Tr}\{\mathbf{d} \cdot e^{-iH't/\hbar} \rho_{r,i,e} \mathbf{d} e^{iH't/\hbar}\}. \tag{2.37}$$

We can take advantage of the fact that the expression inside the trace is the autocorrelation function of the radiator dipole, $C(t)$. Since $\mathbf{d}$ is hermitian, $C(t)$ has the property,

$$C(-t) = C(t)^*, \tag{2.38}$$

we employ the relation above to write $I(\omega)$ as follows,

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i(\omega - i\epsilon)t}\int dv f(v) e^{-i\mathbf{k}\cdot\mathbf{v}t}\mathrm{Tr}\{\mathbf{d}\cdot e^{-iH't/\hbar}\rho_{r,i,e}\mathbf{d}e^{iH't/\hbar}\} \tag{2.39}$$

By evaluating the integral over v and applying the Fourier convolution theorem we arrive at the following expression [48]:

$$I(\omega) = \int_{-\infty}^{\infty}\frac{d\omega'}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(\omega-\omega')^2}{2\sigma^2}\right) I_S(\omega') \tag{2.40}$$

where

$$2\sigma^2 = \frac{\omega'^2}{c^2}\left(\frac{2k_BT}{m_r}\right). \tag{2.41}$$

The lineshape for the radiator in the center of mass frame is given by

$$I_S(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i(\omega-i\epsilon)t}\mathrm{Tr}\{\mathbf{d}\cdot e^{-iH't/\hbar}\rho_{r,i,e}\mathbf{d}e^{iH't/\hbar}\}. \tag{2.42}$$

In the next section, we will the address the problem of Stark broadening due to ions and electrons. For the time being, we will refer to $I_S(\omega)$ in eq. 2.42 as simply $I(\omega)$.

2.5 Stark Broadening Theory

Our theoretical development of $I_s(\omega)$ follows standard methods regarding Stark broadening by perturbing electrons and ions. The current calculation incorporates a model of the plasma that accounts for the motion of the electrons and ions; the latter can have a significant broadening effect at the center of Ar lines when the Ar radiator is immersed in a plasma of relatively lighter ions, such as deuterium, as is the case in ICF implosions. For cases where the ion perturbers are more massive, such as targets filled entirely with higher-Z ions such as Ne, Ar, and Kr, ion dynamic effects are reduced greatly and line-shapes closely resemble those generated with the static-ion approximation [18].

We must now write the full Hamiltonian of the radiator and the plasma electrons and ions, excluding the translational motion of the radiator,

$$H' = H_r + H_i + H_e + V_{i,e} + V_{e,r} + V_{i,r}. \tag{2.43}$$

Here, the first three terms on the r.h.s. refer to the kinetic and potential energies of the respective subsystems, $H_j = T_j + V_j$. The interaction potentials between subsystems j and k are given by $V_{j,k}$. Referring to eq. 2.42, we will define a Liouville operator as a commutator of an arbitrary operator with the Hamiltonian, such that

$$L'\hat{f} = [H', \hat{f}] \qquad \text{and} \qquad e^{-iL't}\hat{f} = e^{-iH't/\hbar}\,\hat{f}\,e^{iH't/\hbar}, \tag{2.44}$$

in order to arrive at the following expression:

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i(\omega - i\epsilon)t}\mathrm{Tr}\{\mathbf{d}\cdot e^{-iL't/\hbar}\rho_{r,i,e}\mathbf{d}\}. \tag{2.45}$$

Since the dipole operator acts only on the radiator internal states, we can bring the trace over plasma states within the brackets.

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\mathrm{Tr}_r\int_0^\infty dt\, e^{i(\omega - i\epsilon)t}\mathbf{d}\cdot\mathrm{Tr}_{i,e}\{e^{-iL't/\hbar}\rho_{r,i,e}\mathbf{d}\} \tag{2.46}$$

Traditionally, the effects of the plasma ions are addressed at this point. Since we will include the effects of ion dynamics, we find it simpler to examine the radiator-plasma electron interactions first. Operators acting on plasma ion coordinates will be indicated with the subscript, $\hat{\mathcal{E}}_i$. The interaction of the plasma electrons with the plasma ions V_{ie} will be included in the plasma ion hamiltonian to account for screening of the plasma ions,

$$H' = H_r + V_{r,\hat{\mathcal{E}}_i} + H_i + H_e + V_{e,r}, \tag{2.47}$$

where

$$V_{r,\hat{\mathcal{E}}_i} = V_{i,r} + V_{i,e}. \tag{2.48}$$

In order to address the effects of the plasma electrons, we will be presenting an electron shift and width operator that was obtained employing standard kinetic theory techniques as described by Hussey [38] and simplified using certain weak coupling limits by Dufty *et al.* [49]. Due to the sheer length and complexity of the formalism, we will present the results of Dufty *et al.* and proceed from that

point. First, we must describe procedures to separate out the effects of the plasma electron interactions in the hamiltonian and the corresponding Liouville operator. The Liouville operator corresponding to a single plasma electron, $L(1)$, can be written as follows,

$$L(1)\hat{f} = [T(1) + V_0(1), \hat{f}], \tag{2.49}$$

where $V_0(1)$ represents the monopole interaction of the electron with the radiating ion, which is dependent on only the perturber coordinates if we treat the center of mass of the radiator as an inertial frame. The interaction potential between an individual plasma electron and the internal states of the radiator, $V_1(r,1)$, can also be expressed in terms of a Liouville operator. In order to account for the screening due to plasma electrons we will also introduce the operator $\mathcal{L}(r,1)$,

$$[L_1(r,1)\hat{f} = [V_1(r,1), \hat{f}\,] \quad \text{and} \quad [\mathcal{L}(r,1)\hat{f} = [V_s(r,1), \hat{f}\,], \tag{2.50}$$

where $V_s(r,1)$ represents the screened interaction potential between the radiator and one perturbing electron.

Using the preceding definitions, the line profile can be expressed as follows:

$$I(\omega) = -\frac{1}{\pi}\mathrm{Im}\mathrm{Tr}_r\mathbf{d} \cdot \mathrm{Tr}_{i,e}R(\omega)f(r,\hat{\mathcal{E}})\mathbf{d}\}, \tag{2.51}$$

where

$$R(\omega)^{-1} = \omega - L(r) - L_1(r,\hat{\mathcal{E}}) - B - M(\omega), \tag{2.52}$$

and $f(r,\hat{\mathcal{E}})$ is a distribution function for the internal radiator states and plasma ion states. The operators B and $M(\omega)$ make up our electron shift and width operator,

which correspond to a mean-field, $\langle L_{er} \rangle_e$, and a fluctuation term $\mathcal{M}_{er}$ respectively. Dufty *et al.* obtained forms for B and $M(\omega)$ similar to the ones below [49],

$$B = n_e \mathrm{Tr}_1 L_1(r,1) f(r1) f(r)^{-1}, \tag{2.53}$$

and

$$M(\omega) = n_e \mathrm{Tr}_1 \mathcal{L}(r,1) f(r1) \{\omega - L(r) - L_1(r,\hat{\mathcal{E}}) - L(1) - \mathcal{L}(r,1)\}^{-1} \mathcal{L}(r,1). \tag{2.54}$$

In Chapter III, we will discuss the operators B and $M(\omega)$ in detail. We will now address the issue of the plasma ion interactions. The assumption that the ions are stationary during the time of interest will not be made. We will follow the formalism introduced by Boercker *et al.*, in ref. [40] and outlined by Griem in ref. [1]. The procedure to separate out the effects of the plasma ions is similar to the one employed to obtain B and $M(\omega)$; however, there are some important distinctions. The plasma ions are treated collectively and their interactions with the radiator are represented by an electric field acting with the radiator dipole moment.

We begin by defining the dipole moment operator, $\tilde{\mathbf{F}}(r,\hat{\mathcal{E}};\omega)$, where the effects of the radiator-plasma electron interactions have already been accounted for,

$$\mathbf{F}(r,\hat{\mathcal{E}};t) = e^{-i\tilde{L}'t} \rho_{r,\hat{\mathcal{E}}} \mathbf{d}, \tag{2.55}$$

where

$$\tilde{L}' = L(r) + L_1(r,\hat{\mathcal{E}}) + B + M. \tag{2.56}$$

We employ a dummy variable $\mathcal{E}$ to represent the microfield due to one of the plasma ion configurations so that the trace over ion coordinates can be expressed as an integral over a microfield distribution function, $Q(\mathcal{E})$, which is shown below,

$$\begin{aligned} \mathrm{Tr}_{\hat{\mathcal{E}}}\mathbf{F}(r,\hat{\mathcal{E}};t) &= \int d\mathcal{E}\mathrm{Tr}_{\hat{\mathcal{E}}}\left[\mathbf{F}(r,\hat{\mathcal{E}};t)\delta(\mathcal{E}-\hat{\mathcal{E}})\right] \\ &= \int d\mathcal{E}Q(\mathcal{E})\mathbf{F}(r,\mathcal{E};t), \end{aligned} \tag{2.57}$$

where

$$\mathbf{F}(r,\mathcal{E};t) = Q(\mathcal{E})^{-1}\mathrm{Tr}_{\hat{\mathcal{E}}}\left[\mathbf{F}(r,\hat{\mathcal{E}};t)\delta(\mathcal{E}-\hat{\mathcal{E}})\right]. \tag{2.58}$$

Using the time dependent Shrödinger equation, we obtain the following dynamical equation:

$$\frac{\partial}{\partial t}\mathbf{F}(r,\mathcal{E};t) + i\left[L(r) + L_1(r,\mathcal{E}) + B + M\right]\mathbf{F}(r,\mathcal{E};t) = \left.\frac{d}{dt}\mathbf{F}(r,\mathcal{E};t)\right|_{ions}, \tag{2.59}$$

where $L_1(r,\mathcal{E})$ is the Liouville operator associated with the radiator interaction with a given microfield $\mathcal{E}$. The term on the right hand side is analogous to the collision term in Boltzmann equation, and hence can be rewritten as

$$\left.\frac{d}{dt}\mathbf{F}(r,\mathcal{E};t)\right|_{ions} = \int d\mathcal{E}'\left[W(\mathcal{E}'\to\mathcal{E})\mathbf{F}(r,\mathcal{E}';t) - W(\mathcal{E}\to\mathcal{E}')\mathbf{F}(r,\mathcal{E};t)\right], \tag{2.60}$$

where $W(\mathcal{E}'\to\mathcal{E})$ represents a transition rate from microfield $\mathcal{E}'$ to $\mathcal{E}$. If we take advantage of the symmetry relations between $W(\mathcal{E}'\to\mathcal{E})$ and $W(\mathcal{E}\to\mathcal{E}')$ and use the simplest choice for Wwe get the following expression:

$$W(\mathcal{E}'\to\mathcal{E}) = \nu Q(\mathcal{E}'), \tag{2.61}$$

so that we may re-express eq. 2.59 as follows:

$$\left[\frac{\partial}{\partial t} + iL(r) + iL_1(r,\mathcal{E}) + iB + iM\right]\mathbf{F}(r,\mathcal{E};t) = -\nu\left[\mathbf{F}(r,\mathcal{E};t) - \int d\mathcal{E}' Q(\mathcal{E}')\mathbf{F}(r,\mathcal{E}';t)\right]. \quad (2.62)$$

where the quantity nu is related to the momentum autocorrelation function. We now take the Laplace transform of $\mathbf{F}(r,\mathcal{E};t)$ to arrive at the following expression:

$$\tilde{\mathbf{F}}(r,\mathcal{E};\omega) = [\mathbf{d} + \nu\mathbf{I}(\omega)][-i\omega + \nu + iL(r) + iL_1(r,\mathcal{E}) + iB + iM(\omega)]^{-1}, \quad (2.63)$$

where

$$\mathbf{I}(\omega) = \int d\mathcal{E}' Q(\mathcal{E}')\tilde{\mathbf{F}}(r,\mathcal{E}';\omega). \quad (2.64)$$

By integrating $\tilde{\mathbf{F}}(r,\mathcal{E};\omega)$ over the microfield distribution and some manipulation , we can obtain an expression for $\mathbf{F}(r,\mathcal{E};\omega)$,

$$\tilde{\mathbf{F}}(r,\mathcal{E};\Delta\omega) = i[\Delta\omega + i\nu - L_1(r,\mathcal{E}) - B - M(\Delta\omega,\mathcal{E})]^{-1}[1 - \nu G(\Delta\omega)]^{-1}\mathbf{d}, \quad (2.65)$$

where

$$G(\Delta\omega) = \int d\mathcal{E} Q(\mathcal{E})\mathcal{R}(\Delta\omega), \quad (2.66)$$

and

$$\mathcal{R}(\Delta\omega) = (\Delta\omega + i\nu - L_1(r,\mathcal{E}) - B - M(\Delta\omega,\mathcal{E}))^{-1}. \quad (2.67)$$

The quantity $\Delta\omega$ is defined as $\omega - L(r)$. The expression for $\mathbf{F}(r, \mathcal{E}; \omega)$ can now be substituted into eq. 2.51 to arrive at the following expression for $I(\omega)$:

$$I(\omega) = -\frac{1}{\pi}\mathrm{Im}\mathrm{Tr}_r \mathbf{d} \cdot [1 - \nu G(\Delta\omega)]^{-1} G(\Delta\omega) f(r, \mathcal{E})\mathbf{d}. \tag{2.68}$$

At this point, the overall lineshape expression is complete, although few assumptions have been made about the form or details of the radiator, plasma ion, or plasma electron Hamiltonian. In the next chapter, we will explore in greater detail the electron shift and width operators, B and $M(\omega)$. We will obtain useful expressions for the operators employing a full Coulomb form of the radiator-plasma electron interaction. We will also address the problem of calculating B and $M(\omega)$ for multi-electron radiators.

CHAPTER 3
THE ELECTRON SHIFT AND WIDTH OPERATOR

In this chapter, we examine the electron shift and width operator in more detail. A form the radiator-perturbing electron interaction potential is introduced and applied to the expressions for B and $M(\omega)$ introduced in Chapter II. We will apply an approximation, second order in the radiator-perturbing electron interaction, to treat highly ionized, moderate-Z radiators. Its validity will be discussed and justified. We then outline the formalism with which we address the problem of line radiation from multi-electron radiators. We present the calculational forms of the first and second order terms of the shift and width operator for very simple multi-electron cases to show the expressions reduce to a form very similar to the hydrogenic case presented by Woltz [13, 14]. Specifically, we examine radiators with no more than two electrons in an upper manifold.

3.1 Radiator-Perturbing Electron Interaction

In order to comment further on the operators B and $M(\Delta\omega)$, we first write the Hamiltonian, H', in which the effects of the radiator-perturbing ion interaction have already been incorporated into the ion microfield:

$$H' = H_r + e\,\mathcal{E}\,Z_r + K_e + V_{er} + V_{ee}. \tag{3.1}$$

The first term on the right hand side is the Hamiltonian for an isolated radiator. In the second term, the effects of the perturbing ions have been expressed in terms of the radiator dipole interacting with the ion microfield. It may seem counter-intuitive to suggest that the dipole approximation is valid for radiator interactions with plasma ions, but invalid for interactions with plasma electrons at high densities. However, for highly charged radiators, the perturbing ions experience a strong repulsion due to the monopole interaction with the radiator, which is included in the microfield calculation. Therefore, the ions remain sufficiently distant from the radiator for the dipole approximation to be valid. Higher order corrections to the dipole approximation have been evaluated and appear to have a relatively small effect [50]. This is not the case for plasma electrons which experience an equally strong attraction and may have the opportunity to penetrate the radiator orbitals. Continuing with the rest of the Hamiltonian, K_e is the kinetic energy of the plasma electrons, V_{er} is the radiator-perturbing electron interaction, and V_{ee} represents the perturbing electron-electron interactions.

In order to calculate B and $M(\Delta\omega)$, the interaction potential between the radiator and a given plasma electron, is divided into a long-range monopole term, $V^{(0)}(j)$, and a short-range interaction, $V^{(1)}(r,j)$, as follows, where $V^{(0)}(j)$ is the monopole interaction of the jth perturbing electron with the radiator, and x_j is the coordinate of that electron,

$$V^{(0)}(j) \;=\; -\frac{(Z-N_r)}{x_j}, \tag{3.2}$$

and $V^{(1)}(r,j)$ is the sum of the interactions between N_r individual radiator electron and the perturbing electron,

$$\begin{aligned} V^{(1)}(r,j) &= \left(\frac{1}{|x_j - x_{r_1}|} - \frac{1}{x_j}\right) + \left(\frac{1}{|x_j - x_{r_2}|} - \frac{1}{x_j}\right) \\ &+ \ \ldots + \left(\frac{1}{|x_j - x_{r_{N_r}}|} - \frac{1}{x_j}\right). \end{aligned} \tag{3.3}$$

The coordinates of the ith radiator electron are denoted by x_{r_i}. Later, we will take advantage of the fact that $V^{(1)}(r,j)$ has been expressed as a sum of symmetric operators on the radiator electron coordinates. $V^{(0)}(j)$ is independent of radiator electron coordinates and may be included in the Hamiltonian of the plasma electrons,

$$H(j) = \frac{p_j^2}{2m} - V^{(0)}(j). \tag{3.4}$$

This form lends itself to employing Coulomb wavefunctions to describe the motion of the perturbing electrons, as was done in the past [12, 13, 14].

We can now define Liouville operators, $L(r,1)$ and $L_1(r,1)$, as follows,

$$L(r,1)\hat{f} = [H'(r,1), \hat{f}] \qquad L_1(r,1)\hat{f} = [V^{(1)}(r,1), \hat{f}], \tag{3.5}$$

where $\hat{f}$ is an arbitrary operator. $H'(r,1)$ represents the Hamiltonian for the radiator interacting with the ion microfield and a single plasma electron.

$$H'(r,1) = H_r + e\,\mathcal{E}\,Z_r + H(1) + V^{(1)}(r,1) \tag{3.6}$$

As was shown in the previous chapter, the electron interaction operators B and $M(\Delta\omega)$ can be expressed in terms of $L(r,1)$ and $L_1(r,1)$ [12, 38, 49].

$$B = n\mathrm{Tr}_1 L_1(r,1) f(r1) f(r)^{-1} \tag{3.7}$$

$$M(\omega) = n\mathrm{Tr}_1 \left[\mathcal{L}(r,1) f(r1)[\omega - L(r) - L_1(r,\mathcal{E}) - L(1) - \mathcal{L}(r,1)]^{-1} \mathcal{L}(r,1) f(r)^{-1}\right], \tag{3.8}$$

where $f(r)$ and $f(r1)$ are distribution functions for the isolated radiator and the radiator-perturbing electron system, respectively. These expressions were derived from an exact expression obtained by Hussey [38, 39] and simplified by Dufty *et al.* [49]. In eq. 3.8 the effect of plasma electron correlations are incorporated by Dufty and Boercker [49], into $\mathcal{L}(r,1)$, which is simply statically shielded forms of $L_1(r,1)$. The quantity, B, represents the time-independent portion of the interaction of the plasma electrons with the radiator corresponding to the initial correlations. It is real and provides the bulk of the shift for the cases under consideration. $M(\omega)$ is the transform of the autocorrelation function of the electron interaction potential $V_1(r,1)$. At this point, B and $M(\omega)$ are exact to all orders in $V_1(r,1)$.

3.2 The Second-Order Approximation

We will calculate B and $M(\omega)$ to second order in the radiator-perturbing electron interaction, $L_1(r,1)$, using a full-Coulomb expression of the interaction potential [12, 51]. There has been some confusion concerning the relationship between the relative size of the first order shift and the shift contribution found by expand-

ing the electron shift and width term in powers of the radiator-plasma electron interaction. The size of the first order term of the shift has little to do with the appropriateness of terminating electron shift- and width operator expansion with the second order term for a given temperature and density. As will be shown later, the first order term has no contribution from the multipole expansion beyond the penetrating monopole term, therefore it is inappropriate to compare its contribution with that from terms containing contributions from the dipole interaction and beyond, in order to determine the appropriateness of the second order treatment. In fact, one could anticipate a case where the first order shift is on the order of the second order term or smaller and yet the second order approximation is valid.

Let us now specify that $B^{(1)}$ represents the effects of the shielding due to plasma electrons penetrating the radiator orbital on the energy of the bound electron with no higher order corrections, then the expression $B - B^{(1)} + M(\Delta\omega)$ represents the corrections to that term. We have rephrased the question to ask whether truncating the electron shift and width operator gives not only a good result for the width but an adequate correction to the shift. In order to apply the second order approximation, two conditions must be satisfied. First, large portions of the broadened lines must satisfy the inequality, $\Delta\omega \lesssim 2\omega_{pe}$, where $\Delta\omega$ is the frequency separation from line center and ω_{pe} is the plasma frequency. This is relevant because second-order calculations have been shown to be valid in this range [51, 52]. Second, the plasma electrons must undergo predominantly weak collisions, which are defined as collisions where the change in the electron's momentum is much smaller than the total momentum. Another way to express this idea is to state the impulse experienced by the perturber is small. The plasmas under consideration must

be characterized by sufficiently high temperatures so that even collisions where the perturbing electron penetrates the bound electron orbital can be described as 'weak.' In other words, the average plasma electron has a large kinetic energy and spends a relatively short time near the radiator itself and thus receives only a small impulse, relative to its momentum. The appropriate temperature regime is defined by,

$$kT > \frac{Z(Z-1)}{n^2}(\text{Ryd}) \quad [30]. \tag{3.9}$$

This expression was obtained by comparing the difference in the kinetic energy of an electron far from the radiator to its value at the point of closest approach.

There are two reasons to believe that the second-order approximation is an appropriate choice. First, large portions of the α-, β-, and γ-lines of K-shell Ar, for the plasma conditions under consideration, satisfy the condition that the width of line be no more than two times the plasma frequency [52]. Second, the β- and γ-lines satisfy the inequality in eq. 3.9 for the temperature conditions observed in recent experiments [20, 22, 21].

It will be shown later in this section that B, the static shift, can be expanded into a term first order in the interaction potential and a term containing all higher order effects [31]. We will outline the process here. We can expand the distribution function, $f(r,1)$, and thus B, in terms of $V^{(1)}(r,1)$. By successively closing kinetic equations in the equilibrium Bogliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, Boercker and Dufty obtained the following expression for $f(r,1)$:

$$f(r,1) = Z\,exp\{-\beta[H(r) + H(1) + V_s(r,1)]\} \quad [49], \tag{3.10}$$

where $V_s(r,1)$ is a statically screened radiator-electron interaction potential. Boercker and Iglesias expanded $f(r,1)$ in orders of $V_s(r,1)$ and obtained expressions for $B^{(1)}$ and $B^{(2)}$ [31, 53]. We begin by making the following definitions:

$$H'_0 = H(r) + H(1), \qquad V_1 = V_s(r,1). \tag{3.11}$$

We express the distribution function in terms of H'_0 and a "development operator" $\mathcal{U}(\beta,0)$,

$$e^{-\beta H'} = e^{-\beta H'_0}\mathcal{U}(\beta,0) \qquad \text{and} \qquad V_1(\tau) = e^{\tau H'_0}V_1 e^{-\tau H'_0}, \tag{3.12}$$

where $\mathcal{U}(\beta,0)$ is defined as follows:

$$\mathcal{U}(\beta,0) = \sum_{n=0}^{\infty}(-1)^n\frac{1}{n!}\int_0^\beta d\tau_1\cdots\int_0^\beta d\tau_n \mathrm{T}_\beta[V_1(\tau_1)\cdots V_1(\tau_n)]. \tag{3.13}$$

$\mathcal{U}$ will be approximated to first order in V_1:

$$\mathcal{U}(\beta,0) = 1 - \int_0^\beta d\tau e^{\tau H'_0}V_1 e^{-\tau H'_0} + \mathcal{O}(V_1)^2. \tag{3.14}$$

This approximation is possible only if the integral over τ is much smaller than one. Since τ is no larger than kT^{-1}, the average interaction potential must be no larger than kT.

If we define $f_0(r)$ and $f_0(1)$ using the following equations,

$$f_0(r) = Z_r\, e^{-\beta H(r)} \qquad \text{and} \qquad f_0(1) = Z_e\, e^{-\beta H(1)}, \tag{3.15}$$

where Z_r and Z_e are the respective partition functions for $f_0(r)$ and $f_0(1)$, we can re-express $f(r,1)$ in terms of $f_0(r)$ and $f(1)$ and $\mathcal{U}(\beta,0)$.

$$f(r,1) = f_0(r)f_0(1)\mathcal{U}(\beta,0). \tag{3.16}$$

If we substitute this expression into eq. 3.7 using the expression for $\mathcal{U}(\beta,0)$ from eq. 3.14, we arrive at the following expressions for $B^{(1)}$ and $B^{(2)}$:

$$B^{(1)} = n\mathrm{Tr}_1[L_1(r,1)f_0(1)], \tag{3.17}$$

$$B^{(2)} = -n\mathrm{Tr}_1\{L_1(r,1)f_0(r)f_0(1) \times \int_0^\beta d\tau e^{\tau[H(r)+H(1)]}V_s(r,1)e^{-\tau[H(r)+H(1)]}f_0(r)^{-1}\}. \tag{3.18}$$

Starting with eqs. 3.17 and 3.18, we can express the trace over perturber states in terms of integrals over perturber momenta. We introduce complete sets of radiator eigenstates to obtain a matrix representation, and evaluate the integral over τ. All of this is described in detail in Appendix B. We rewrite eqs. B.8 and B.13 below,

$$B^{(1)} = n\lambda_T^3 \int d\mathbf{k} e^{-\frac{\beta k^2\hbar^2}{2m}} \left[\langle\mu;\mathbf{k}|V_1(r,1)|\mu';\mathbf{k}\rangle\delta_{\nu\nu'} - B^{(1)}_{\nu\nu'}\delta_{\mu\mu'}\right] \tag{3.19}$$

$$B^{(2)}_{\mu\nu\mu'\nu'} = -n\int d\mathbf{k}_1 \int d\mathbf{k}_2 \sum_{\mu''} \langle\mu\mathbf{k}_1|V_1(r,1)|\mu''\mathbf{k}_2\rangle\langle\mu''\mathbf{k}_2|V_s(r,1)|\mu'\mathbf{k}_1\rangle f_0(\mu'') \times f_0(k_2)f_0(\mu')^{-1}\frac{\left(\exp\{\beta[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m} - \frac{k_1^2\hbar^2}{2m}]\} - 1\right)}{[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m} - \frac{k_1^2\hbar^2}{2m}]}\delta_{\nu\nu'} + O.T., \tag{3.20}$$

where μ and ν represent arbitrary radiator states, and $\mathbf{k}$ represents the wavenumber of the perturber state. $B^{(1)}_{\nu\nu'}$ has the same form as the first term but the matrix

element is between states ν and ν'. Also, $O.T$ refers to a second term in $B^{(2)}$ where the one of the matrix elements is between states ν and ν'. For the sake of brevity, we will examine only this first term for now. We next make an approximation in order to express the matrix elements in terms of initial and final radiator states.

Since B is a tetradic operator acting on the radiator dipole, $\mathbf{d}$, it can be written in the following form:

$$[B\mathbf{d}]_{\mu\nu} = \sum_{\mu'\nu'} B_{\mu\nu\mu'\nu'}\mathbf{d}_{\mu'\nu'}. \tag{3.21}$$

We will assume that initial and final states of the radiative transition are sufficiently separated in energy so that the matrix elements of $V_1(r,1)$ between initial and final states are negligible compared to matrix elements among initial states or among final states. This is the "No Quenching" approximation; we assume there are no non-radiative transitions between initial and final states. Therefore, since the radiator dipole must act between an initial and final state, we will substitute $|i\rangle$ for $|\mu\rangle$ and $|f\rangle$ for $|\nu\rangle$. The matrix elements of the radiator-perturbing electron interaction $V_1(r,1)$ between initial and final states will be assumed to equal zero. Below, we have re-expressed eqs. B.8 and B.13 using a partial wave expansion for the perturber states,

$$\begin{aligned} B^{(1)}_{if'i'f'} &= n\lambda_T^3 \int dk\, k^2 e^{-\beta\frac{\hbar^2k^2}{2m}} \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \{\langle i;k,l,m|V^{(1)}(r,1)|i';k,l,m\rangle\delta_{ff'} \\ &\quad -\langle f;k,l,m|V^{(1)}(r,1)|f';k,l,m\rangle\delta_{ii'}\} \end{aligned} \tag{3.22}$$

and

$$B^{(2)}_{i_f i'_f f'} = -\delta_{ff'} n \lambda_T^3 \int dk_1 \int dk_2 \sum_{i''} D_{i,i'',i'}(k_1,k_2) \times \frac{\exp\left[-\beta\frac{\hbar^2 k_1^2}{2m}\right] - \exp\left[-\beta(\frac{\hbar^2 k_2^2}{2m} + \hbar\omega_{i''} - \hbar\omega_{i'_f})\right]}{(\hbar\omega_{i''} - \hbar\omega_{i'_f} + \frac{\hbar^2 k_2^2}{2m} - \frac{\hbar^2 k_1^2}{2m})}, \quad (3.23)$$

where

$$D_{i,i'',i'}(k_1,k_2) = k_1^2 k_2^2 \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} \langle i;k_1,l_1,m_1|V_s(r,1)|i'';k_2,l_2,m_2\rangle \langle i'';k_2,l_2,m_2|V_s(r,1)|i';k_1,l_1,m_1\rangle. \quad (3.24)$$

All the information about the matrix elements of the interaction potential for the second order term is contained in $D_{i,i'',i'}(k_1,k_2)$, which we will put in calculable form in Section3.5. The product 'ket' of the initial radiator state, i, and the perturbing electron state are represented by $|i;k,l,m\rangle$ The plasma electron state is represented by a partial wave expansion, where l and m describe the angular momentum state, and k is the wave number defined as follows:

$$H(1)|k,l,m\rangle = \frac{\hbar^2 k^2}{2m}|k,l,m\rangle. \quad (3.25)$$

Returning to eq. 3.8, we see that $M(\omega)$ is already at least second order in $\mathcal{L}(r,1)$, the screened form of $L_1(r,1)$. For a strictly second order form of $M(\omega)$, the expression $L(r) + L(1) + \mathcal{L}(r,1)$ in the resolvent should be substituted with $L(r)+L(1)$. However, we will instead employ $L(r)+L(1)+B^{(1)}$, since the first order shift provides a non-perturbative modification of the energy levels, with respect to

the plasma frequency; therefore, this is not strictly a second order expression. In the form presented below, the term, $M(\Delta\omega)_{i,i'}$, which describes the interaction of the initial states, is re-expressed as a integral over time. There is a corresponding term for the interaction of the final states, as well as interference terms that are written in eq. B.23,

$$\begin{aligned} M(\omega)_{ii'} &= -in\lambda_T^3 \int dk_1 e^{-\beta\frac{\hbar^2 k_2^2}{2m}} \int dk_2 \int dt \sum_{i''} D_{i,i'',i'}(k_1,k_2) \\ &\quad \times exp\{i(\hbar\Delta\omega_{i''f} - B^{(1)}_{i''f} + \frac{\hbar^2 k_1^2}{2m} - \frac{\hbar^2 k_2^2}{2m} + i\epsilon)t\}\delta_{ff'}. \end{aligned} \tag{3.26}$$

While the quantities, $B^{(1)}$ and $B^{(2)}$ are real and contribute only to the shift, the dynamic term, $M(\Delta\omega)$, is complex. It contributes to both the shift and width. We now evaluate the integral over time, remembering that we are taking the limit as $\epsilon \to 0$,

$$\begin{aligned} -i\int_0^\infty dt\, e^{i[f(\omega)+i\epsilon]t} &= \lim_{\epsilon\to 0^+} \frac{1}{[f(\omega)+i\epsilon]}, \\ &= \lim_{\epsilon\to 0^+} \frac{f(\omega)-i\epsilon}{[f(\omega)]^2+\epsilon^2}, \\ -i\int_0^\infty dt\, e^{i[f(\omega)+i\epsilon]t} &= \mathrm{P}\frac{1}{f(\omega)} - i\pi\delta(f(\omega)). \end{aligned} \tag{3.27}$$

where P stands for the Cauchy principle part. It is relatively straightforward to evaluate the imaginary part of $M(\Delta\omega)$. Following the methods of O'Brien and Hooper [10], we will use the following relation, where F is a function of k, to evaluate the integral of the real part of $M(\Delta\omega)$:

$$\mathrm{P}\int_0^\infty dk\, \frac{F([k_0^2+\omega]^{1/2})}{\omega + k_0^2 - k^2} = 0, \qquad \omega > 0. \tag{3.28}$$

Using the expression above, we get the following expressions for $\Delta\omega_{i''f} > 0$, with similar expressions for $\Delta\omega_{i''f} < 0$:

$$\mathrm{Re}M(\omega)_{ii'} = \frac{4n\lambda_T^3}{\pi^2}\sum_{i''}\int dk_1 \int dk_2 (\hbar\Delta\omega_{i''f} + \frac{\hbar^2}{2m}(k_1^2 - k_2^2))^{-1}$$
$$\left[e^{-\beta\frac{\hbar^2k_2^2}{2m}} D_{i,i'',i'}(k_1,k_2) - e^{-\beta\left(\frac{\hbar^2k_1^2}{2m}+\hbar\Delta\omega_{i''f}\right)} D_{i,i'',i'}\left(k_1, \left(k_1^2 + \frac{2m\Delta\omega_{i''f}}{\hbar}\right)^{1/2}\right)\right], \quad \Delta\omega_{i''f} > 0, \tag{3.29}$$

$$\mathrm{Re}M(\omega)_{ii'} = \frac{4n\lambda_T^3}{\pi^2}\sum_{i''}\int dk_1 \int dk_2 (\hbar\Delta\omega_{i''f} + \frac{\hbar^2}{2m}(k_1^2 - k_2^2))^{-1}$$
$$e^{-\beta\frac{\hbar^2k_2^2}{2m}}\left[D_{i,i'',i'}(k_1,k_2) - D_{i,i'',i'}\left(\left(k_2^2 + \frac{2m|\Delta\omega_{i''f}|}{\hbar}\right)^{1/2}, k_2\right)\right], \quad \Delta\omega_{i''f} < 0, \tag{3.30}$$

$$\mathrm{Im}M(\omega)_{ii'} = -\frac{4n\lambda_T^3}{\pi^2}\frac{m\pi}{\hbar}\sum_{i''}\int dk_1 e^{-\beta\left(\frac{\hbar^2k_1^2}{2m}+\hbar\Delta\omega_{i''f}\right)} \frac{D_{i,i'',i'}\left(k_1, \left(k_1^2 + \frac{2m\Delta\omega_{i''f}}{\hbar}\right)^{1/2}\right)}{\left(k_1^2 + \frac{2m\Delta\omega_{i''f}}{\hbar}\right)^{1/2}}. \quad \Delta\omega_{i''f} > 0, \tag{3.31}$$

$$\mathrm{Im}M(\omega)_{ii'} = -\frac{4n\lambda_T^3}{\pi^2}\frac{m\pi}{\hbar}\sum_{i''}\int dk_2 e^{-\beta\left(\frac{\hbar^2k_2^2}{2m}\right)} \frac{D_{i,i'',i'}\left(\left(k_2^2 + \frac{2m|\Delta\omega_{i''f}|}{\hbar}\right)^{1/2}, k_2\right)}{\left(k_2^2 + \frac{2m|\Delta\omega_{i''f}|}{\hbar}\right)^{1/2}}. \quad \Delta\omega_{i''f} < 0. \tag{3.32}$$

We now have expressions for the width and shift operator to second order in the radiator-perturber interaction potential in terms of the matrix elements of that

interaction. The next step involves obtaining calculable forms of the single matrix element in $B^{(1)}$ and the expression $D_{i,i'',i'}(k_1,k_2)$ for $B^{(2)}$ and $M(\Delta\omega)$

Boercker and Iglesias showed for neutral radiators that there is significant cancelation in the portion of the shift term which is second order in the interaction potential, between $B^{(2)}$ and $\mathrm{Re}M(\omega)$. They find the real portion of $M(0)$ equals $-\frac{1}{2}B^{(2)}$. This is important for the neutral case, where the first order term is believed to vanish [31]. It can be shown that the second-order behavior is the same for charged radiators; however, the resulting cancelation is a relatively small effect for highly-charged radiators, since the first order shift is dominant.

So far, our expressions have not specified the details of the interaction. In the next section, we will address the challenges of calculating the matrix element, $\langle i,k_1,l_1,m_1|V^{(1)}(r,1)|i';k_2,l_2,m_2\rangle$, for a multi-electron radiator.

3.3 Multi-Electron Formalism

In equations 3.23 and 3.26, the ket $|i;k,l,m\rangle$ represents a direct product of the energy eigenstates for the radiator and perturbing electron. However, since the interaction potential $V_1(r,1)$ does not act on the spin, the matrix elements of the interactions are easiest to calculate in the $\mathcal{LS}$ representation using product wavefunctions for the radiator electrons. Some multi-electron atom- and ion configurations can experience intermediate coupling between angular momentum states. Hence, in order to calculate the matrix elements of the interactions, it is necessary to first transform from the energy eigenstates to specific electron configurations in the $\mathcal{LS}$ representation. A transformation matrix can be obtained by diagonalizing the matrix of the isolated radiator Hamiltonian but retaining the eigenvectors for

the particular representation most useful for the model. Since Cowan does not provide a specific notation for this transformation matrix, we shall refer to it as $\mathbf{T}_{\alpha,i}$. The subscript, α, refers to all the relevant quantum numbers, except $\mathcal{J}$ and $\mathcal{M}$ which represent the total angular momentum and its azimuthal component, of a given configuration in the appropriate representation. We shall employ the geneological $\mathcal{LS}$ basis to express the states of the angular momenta. This representation is described in Appendix C and in Section 4.10 of Cowan's book, *The Theory of Atomic Structure and Spectra*, 1981 [54]. We note that for an isolated radiator the potential is spherically symmetric, and the total angular momentum is conserved. Therefore, $\mathbf{T}_{\alpha,i}$ is block diagonal in $\mathcal{J}$ and invariant in $\mathcal{M}$. We will designate individual blocks by $\mathbf{T}_{\alpha,i}(\mathcal{J})$ and the relevant basis states by $|\Psi_\alpha\rangle_{\mathcal{JM}}$. Therefore, the ith wavefunction, $|i\rangle_{\mathcal{JM}}$, in the energy basis can be expressed as follows:

$$|i\rangle_{\mathcal{JM}} = \sum_{\alpha} |\Psi_\alpha\rangle_{\mathcal{JM}} \mathbf{T}_{\alpha,i}(\mathcal{J}). \tag{3.33}$$

This results in the following matrix elements of the radiator-perturbing electron interaction:

$$\begin{aligned} &{}_{\mathcal{JM}}\langle i; k_1, l_1, m_1 | V_s(r,1) | i'; k_2, l_2, m_2 \rangle_{\mathcal{J}'\mathcal{M}'} \\ &= \sum_{\alpha,\alpha'} \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) {}_{\mathcal{JM}}\langle \Psi_\alpha; k_1, l_1, m_1 | V_s(r,1) | \Psi_{\alpha'}; k_2, l_2, m_2 \rangle_{\mathcal{J}'\mathcal{M}'} \mathbf{T}_{\alpha',i'}(\mathcal{J}') \end{aligned} \tag{3.34}$$

In order to calculate the matrix elements of the interaction, it is important to remember that $V^{(1)}(r,1)$ was defined in eq. 3.3 as a sum of symmetric, one-electron operators. This allows us to employ tools described in detail in Cowan [54]. The first step is to express our interaction in terms of reduced matrix elements.

$V^{(1)}(r,1)$ can be expressed as a multipole expansion in terms of reduced tensor operators for each radiator electron coordinate, x_{r_j},

$$V^{(1)}(r_j,1) = \sum_{t=0}^{\infty} \sum_{q=-t}^{t} A^t(x_{r_j},x_1) C_q^{(t)}(\hat{x}_{r_j}) C_q^{(t)*}(\hat{x}_1), \tag{3.35}$$

where A^t and $C_q^{(t)}$ describe the radial and angular portions of the multipole expansion.

$$A_j^t = \left(\frac{x_<^t}{x_>^{t+1}} - \frac{\delta_{t,0}}{x_1} \right) \qquad C_q^{(t)}(\theta,\phi) \equiv \left(\frac{4\pi}{2t+1} \right)^{1/2} Y_{1q}(\theta,\phi), \tag{3.36}$$

where x_1 is the plasma electron coordinate. $x_<$ and $x_>$ are the lesser or greater, respectively, of the perturbing electron coordinates and relevant radiator electron coordinates. In order to account for screening due to electron correlations, we will follow the usual practice of introducing a cutoff at the Debye length when we integrate over the perturbing electron coordinates. One may also use alternative methods, such as introducing an exponential dependent on the Debye length to the potential, but the choice of a cutoff allows us to compare our results more consistently with other calculations that also employed a cutoff. Please note that the interaction in $B^{(1)}$ is not screened and does not need a cutoff. In our next step, we employ the Wigner-Eckart theorem to obtain reduced matrix elements [55, 56]. We will express our potential as a product of operators dependent on either perturbing electron or radiator coordinates so that we may evaluate the matrix elements independently, this may not always be possible for other potentials, but it is necessary to be able to evaluate the angular portions of matrix elements separately. We have already expressed our perturber wavefunctions in terms of a

partial wave expansion and now apply the Wigner-Eckart theorem [55, 56],

$$
\begin{aligned}
&{}_{\mathcal{J}\mathcal{M}}\langle\Psi_\alpha; k_1, l_1, m_1|V_s(r,1)|\Psi_{\alpha'}; k_2, l_2, m_2\rangle_{\mathcal{J}'\mathcal{M}'} \\
&\quad = \sum_{l_1,l_2}\sum_{t,q}\langle\Psi_{\alpha,\mathcal{J}}||\sum_{j=1}^{N_r} A'^t_j C^{(t)}_j||\Psi_{\alpha',\mathcal{J}'}\rangle\langle k_1,l_1||A'^t_1 C^{(t)}_1||k_2,l_2\rangle \times \\
&\quad (-1)^{\mathcal{J}-\mathcal{M}+l_1-m_1+q}\begin{pmatrix} \mathcal{J} & t & \mathcal{J}' \\ -\mathcal{M} & q & \mathcal{M}' \end{pmatrix}\begin{pmatrix} l_1 & t & l_2 \\ -m_1 & -q & m_2 \end{pmatrix} \quad (3.37)
\end{aligned}
$$

where we have the used the relation,

$$C^{(t)*}_q = (-1)^q C^{(t)}_{-q}. \tag{3.38}$$

The quantity A'^t_j represents the portion of $A^t_{j,1}$ dependent only on the coordinates of the jth radiator electron and A'^t_1 is the portion of $A^t_{j,1}$ dependent on the perturber coordinates. The manner in which the first reduced matrix element is evaluated depends on whether states α and α' are in the same electron configuration. The configuration of a given states is designated only by the number of electrons in each subshell w_s, in which the subshells are in turn are denoted by their principle quantum number $n_s$and orbital angular momentum l_s, for example $4s2p1s$ or $3d1s^2$. If two states are in the same configuration, the matrix elements between them are not strictly diagonal, since the sums of the angular momenta will vary. In the cases where we evaluate a matrix element between states with the same configuration, we will obtain contributions to our calculational result from every occupied subshell. We refer to eq. 9.80 from Cowan [54], since our interaction potential is represented

as a sum over symmetric, one-electron operators,

$$\langle \Psi_{\alpha,\mathcal{J}} | \sum_{j=1}^{n_r} F_j | \Psi_{\alpha,\mathcal{J}} \rangle = \sum_{s=1}^{q} w_s \langle \Psi_{\alpha,\mathcal{J}} | F_s | \Psi_{\alpha,\mathcal{J}} \rangle, \tag{3.39}$$

where s refers to the sum over relevant bound subshells, w_s represents the occupation number of the subshell, q is the total number of relevant subshells, F_s acts on the last electron coordinate in subshell s, and $\Psi_{\alpha,\mathcal{J}}$ is a coupled product function with basic unpermuted coordinate ordering. In order to evaluate matrix elements over the individual subshells we must first uncouple the total spin $\mathcal{S}_q$ from the orbital angular momentum $\mathcal{L}_q$. In order to understand how the angular momentum of the individual subshell L_s is uncoupled from the total we must know how the momenta are originally summed. We employ the geneological LS representation, where the orbital angular momenta of the electrons in a given subshell l_s are summed to obtain the total for that subshell L_s. Then the total momentum for that subshell is added to the intermediate total orbital angular momentum including the previous subshell $\mathcal{L}_{s-1}$ to obtain the new intermediate total, $\mathcal{L}_s$. In order to evaluate the matrix element for a specific subshell, we reverse the process by successively uncoupling the orbital angular momentum of each subshell from the total orbital angular momentum and the intermediate totals. Finally, we uncouple the last electron coordinate l_s from the total for that subshell.

For the case in which α and α' are not in the same configuration, we may apply the methods used by Cowan to calculate general transition arrays. This is achieved by employing a process similar to that described for the previous case. It is a tedious but tractable process of accounting for coordinate permutations and

uncoupling or recoupling angular momenta that can be expressed by a series of factors, which Cowan denotes as D_1 through D_7. One may refer to Appendix C for more details. Here, we show only an abbreviated form similar to eq. 14.78 in Cowan [54],

$$\langle \Psi_{\alpha,\mathcal{J}} || \sum_{j=1}^{N_r} A_r'^t C_r^{(t)} || \Psi_{\alpha',\mathcal{J}'} \rangle = D_1 \cdot D_2 \cdots D_7 \cdot \langle n_i, l_i || A'^t C^{(t)} || n_j, l_j \rangle \quad (3.40)$$

where

$$\begin{aligned} A^{(t)}_{nl,n'l'}(x_1) &= \langle n_i, l_i || A'^t || n_j, l_j \rangle \cdot A_1'^{(t)}(x_1) \\ &= \int dx_r \, x_r^2 R^*_{n_i,l_i}(x_r) \left(\frac{x_<^t}{x_>^{t+1}} - \frac{\delta_{t,0}}{x_1} \right) R_{n_j,l_j}(x_r). \end{aligned} \quad (3.41)$$

The indices, i and j, refer to the subshells relevant to the one-electron transitions. The quantity, $A^{(t)}_{nl,n'l'}(x_1)$, in eq. 3.41, is an expression for the matrix element of the tth term in the multipole expansion of the interaction, $V^{(1)}(r,1)$, integrated over the radiator state of a single bound electron. $R_{n,l}(x_r)$ is the relativistic wave function of the bound electron extracted from Cowan's atomic physics code.

At this point, we will explore the details of evaluating the simplest term of our electron shift and width operator, $B^{(1)}$.

3.4 Evaluation of $B^{(1)}$

We will now attempt simplifications of the expression for $B^{(1)}$ made possible by the trace over perturbing electron states. Let us begin with eq. 3.37 and substitute this expression into $B^{(1)}$ using eq. 3.22, disregarding for the moment the term

acting on the lower states. We will apply the Wigner-Eckart Theorem to the matrix elements of the perturbing electron states,

$$B^{(1)}_{ij i' j'} = \delta_{jj'} n \lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_{l,m} \sum_{t,q} (-1)^{l-m+q} \begin{pmatrix} l & t & l \\ -m & -q & m \end{pmatrix} \times$$
$$\mathbf{T}^{\dagger}_{i,\alpha} \langle \Psi_{\alpha,\mathcal{J}\mathcal{M}} | \sum_{j=1}^{N_r} A'^{t}(j) C^{(t)}_{q}(j) | \Psi_{\alpha',\mathcal{J}'\mathcal{M}'} \rangle \langle k,l || A'^{t}_{1} C^{(t)}_{1} || k,l \rangle \mathbf{T}_{\alpha' i'} (\mathcal{J}'). \quad (3.42)$$

Since the 3-j symbol can only be non-zero when $m_1 - m_1 + q = 0$, q must equal zero, and we can employ Eq. A.8 to sum over m,

$$\sum_{m} (-1)^{l-m+2l+t} \begin{pmatrix} l & l & t \\ m & -m & 0 \end{pmatrix} = \delta_{t0} (-1)^{t} [l]^{1/2}. \quad (3.43)$$

This expression shows that the index, t, of the multipole expansion, must equal zero. In other words, only the monopole interaction between the radiator electrons and the perturbing electrons contributes to the first order shift. We can now re-express $B^{(1)}$ in terms of the reduced matrix element of the monopole interaction.

$$B^{(1)}_{ij i' j'} = \delta_{jj'} n \lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_{l} \delta_{t0} [l]^{1/2} \times$$
$$\mathbf{T}^{\dagger}_{i,\alpha} \langle \Psi_{\alpha,\mathcal{J}\mathcal{M}} | \sum_{j=1}^{N_r} A'^{0}(j) C^{(0)}_{0}(j) | \Psi_{\alpha',\mathcal{J}'\mathcal{M}'} \rangle \langle k,l || A'^{0}_{1} C^{(0)}_{1} || k,l \rangle \mathbf{T}_{\alpha' i'} (\mathcal{J}') \quad (3.44)$$

We now apply the Wigner-Eckart theorem to the matrix elements of the radiator states, and simplify:

$$B^{(1)}_{ij i'j'} = \delta_{jj'} n\lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_l \delta_{l0} [l]^{1/2} (-1)^{\mathcal{J}-\mathcal{M}} \begin{pmatrix} \mathcal{J} & 0 & \mathcal{J}' \\ -\mathcal{M} & 0 & \mathcal{M}' \end{pmatrix} \times$$
$$\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \langle \Psi_{\alpha,\mathcal{J}} || \sum_{j=1}^{N_r} A'^0(j) C^{(0)}(j) || \Psi_{\alpha',\mathcal{J}'} \rangle \langle k, l || A'^0_1 C^{(0)}_1 || k, l \rangle \mathbf{T}_{\alpha',i'}(\mathcal{J}'). \quad (3.45)$$

We use the identity in eq. A.5 to simplify the expression further,

$$\begin{pmatrix} \mathcal{J} & 0 & \mathcal{J}' \\ -\mathcal{M} & 0 & \mathcal{M}' \end{pmatrix} = (-1)^{\mathcal{J}-\mathcal{M}} \delta_{\mathcal{J}\mathcal{J}'} \delta_{\mathcal{M}\mathcal{M}'} [\mathcal{J}]^{-1/2}, \quad (3.46)$$

so that

$$B^{(1)}_{ij i'j'} = \delta_{jj'} \delta_{\mathcal{J}\mathcal{J}'} \delta_{\mathcal{M}\mathcal{M}'} n\lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_l \delta_{l0} \frac{[l]^{1/2}}{[\mathcal{J}]^{1/2}} \quad (3.47)$$
$$\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \langle \Psi_{\alpha,\mathcal{J}} || \sum_{j=1}^{N_r} A'^0(j) C^{(0)}(j) || \Psi_{\alpha',\mathcal{J}} \rangle \langle k, l || A'^0_1 C^{(0)}_1 || k, l \rangle \mathbf{T}_{\alpha',i'}(\mathcal{J}).$$

We must now consider the two cases for which we calculate the reduced matrix elements over the radiator states. First, when the matrix elements are between states in the same configuration we will define an operator similar to $D_1 \cdots D_7$,

$$\langle \Psi_{\alpha,\mathcal{J}} || w_s A'^0(s) C^{(0)}(s) || \Psi_{\alpha',\mathcal{J}'} \rangle = D(s) \langle n_s l_s || w_s A'^0(s) C^{(0)}(s) || n_s l_s \rangle. \quad (3.48)$$

Using eqs. 3.47 and 3.48, we get the following expression:

$$B^{(1)}_{if'i'f'} = \delta_{ff'} n\lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_l \delta_{\mathcal{J}\mathcal{J}'}\delta_{\mathcal{M}\mathcal{M}'}\delta_{t0} \frac{[l]^{1/2}}{[\mathcal{J}]^{1/2}} \times$$
$$\sum_{s=1}^{q} \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) D(s) \langle n_s l_s || w_s A'^0(s) C^{(0)}(s) || n_s l_s \rangle \langle k,l || A'^0_1 C^{(0)}_1 || k,l \rangle \mathbf{T}_{\alpha',i'}(\mathcal{J}). \quad (3.49)$$

We refer to Appendix D regarding our calculation of the angular term. For the case when α and α' are in the same configuration, we arrive at very simple solution, $\alpha = \alpha'$, and the factor obtained from eq. D.9 is written below:

$$D(s) = \delta_{\alpha\alpha'} \frac{[\mathcal{J}_q]^{1/2}}{[l_s]^{1/2}}. \quad (3.50)$$

If we now factor out the reduced matrix elements of $C^{(0)}(s)$ and $C^{(0)}(1)$, we can use the identity written in eq. A.12. Also, we combine $A'^0(s)$ and A'^0_1 into $A^0_{n_s l_s, n_s l_s}(s,1)$, as it was defined in 3.41. So we can write,

$$B^{(1)}_{if'i'f'} = \delta_{ff'}\delta_{\alpha\alpha'}\delta_{\mathcal{J}\mathcal{J}'}\delta_{\mathcal{M}\mathcal{M}'}\delta_{t0} n\lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \times$$
$$\sum_l [l] \sum_{s=1}^{q} w_s \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \langle k,l || A^0_{n_s l_s, n_s l_s}(1) || k,l \rangle \mathbf{T}_{\alpha,i'}(\mathcal{J}'). \quad (3.51)$$

Now we will consider the second case, where states α and α' are not in the same configuration:

$$B^{(1)}_{if'i'f'} = \delta_{\mathcal{J}\mathcal{J}'}\delta_{\mathcal{M}\mathcal{M}'}\delta_{t0}\delta_{ff'} n\lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_l \frac{[l]^{1/2}}{[\mathcal{J}]^{1/2}} \times$$
$$\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) D_1 \cdots D_7 \langle n_i l_i || A'^0 C^{(0)} || n_j l_j \rangle \langle k,l || A'^0_1 C^{(0)}_1 || k,l \rangle \mathbf{T}_{\alpha',i'}(\mathcal{J}) \quad (3.52)$$

If we factor out the reduced matrix element $\langle l_i||C^{(0)}||l_j\rangle$, according to eq. A.12, we find that $l_i = l_j$, where l_i is the orbital angular momentum of the electron undergoing the transition in state α and l_j is the angular momentum of the same electron in state α'. Since the electron must be in the same angular momentum state, it must change principle quantum number in order to undergo a transition. Since all the other radiator electrons do not undergo transitions α and α' are members of a Rydberg series, for example, $3s1s^2$ and $4s1s^2$. If we do not consider matrix elements where electrons undergo transitions between manifolds of differing principal quantum number, only the diagonal matrix elements remain. The second case will be useful for examining cross terms between manifolds, and will be examined in detail in Appendix D. For the hydrogenic- or near hydrogenic case, in the sense that there may be no more than one electron in a non-closed subshell and no more than one electron in the upper manifolds, the factors $D_1 \cdots D_7$ reduce to

$$D_1 \cdots D_7 = \frac{[\mathcal{J}]^{1/2}}{[l_i]^{1/2}} \prod_{s\neq i\neq j}^{q} \delta_{\alpha_s\alpha'_s}. \tag{3.53}$$

Although the factor $[\mathcal{J}]^{1/2}/[l]^{1/2}$ is common to both cases, the diagonal terms contain contributions from each occupied subshell, while only the subshells containing the electron undergoing the transition contribute to the off-diagonal terms. We can now express $B^{(1)}$ in a more familiar form; we will represent the perturber states in terms of Coulomb wavefunctions, $F_l(\eta, kx_1)$, where l is quantum number representing the angular momenta in the partial wave expansion and k is the wavenumber

of the perturber momentum [57]. Then,

$$\langle x|k,l\rangle = \frac{4\pi}{(2\pi)^{\frac{3}{2}}} i^l e^{i\sigma(l,k)} \frac{1}{kx} F_l(\eta, kx). \tag{3.54}$$

where

$$\sigma(l,k) = \arg\Gamma(l+1+i\eta) \qquad \eta = -\frac{Z-1}{ka_0}. \tag{3.55}$$

With some simplifications, we arrive at the following expressions from which $B^{(1)}$ was calculated in this chapter; first,the diagonal term,

$$\begin{aligned} B^{(1)}_{if'f'} &= \frac{2}{\pi} n\lambda_T^3 \sum_{\alpha} \sum_{l=0}^{\infty} \delta_{\alpha,\alpha'} \delta_{t,0} \delta_{ff'} \int dk\, e^{-\beta k^2} (2l+1) \times \\ &\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \int dx_1 F_l(\eta, kx_1) \sum_{s=1}^{q} w_s A^0_{nl_s,nl_s}(x_1) F_l(\eta, kx_1) \mathbf{T}_{\alpha,i'}(\mathcal{J}) - B^{(1)}_{ff'} \delta_{ii'}. \end{aligned} \tag{3.56}$$

Next, the cross term,

$$\begin{aligned} B^{(1)}_{if'f'} &= \frac{2}{\pi} n\lambda_T^3 \sum_{\alpha,\alpha'} \sum_{l=0}^{\infty} \delta_{t,0} \delta_{ff'} \prod_{s\neq i\neq j} \delta_{\alpha_s,\alpha'_s} \int dk\, e^{-\beta k^2} (2l+1) \times \\ &\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \int dx_1 F_l(\eta, kx_1) A^0_{n_i l_i, n_j l_i}(x_1) F_l(\eta, kx_1) \mathbf{T}_{\alpha',i'}(\mathcal{J}) - B^{(1)}_{ff'} \delta_{ii'} \end{aligned} \tag{3.57}$$

where

$$A^0_{n_i l_i, n_j l_i}(x_1) = \int dx_r\, x_r^2 R^*_{n_i,l_i}(x_r) \left(\frac{1}{x_r} - \frac{1}{x_1}\right) R_{n_j,l_j}(x_r). \tag{3.58}$$

$$x_1 < x_r$$

We have arrived at useful expressions for $B^{(1)}$ for multi-electron cases, including a cross term for simple cases. There are two results one should remember from

this section. First, only the monopole term of the multipole expansion contributes to the first order shift, and only if the plasma electron is within the radiator orbital. This suggests that the first order term represents an average shielding of the radiator electron, lowering the effective ion nuclear charge, Z. Second, there can be non-negligible interactions between states of differing principal quantum number. If adjacent levels are sufficiently close, the shift of the composite lines may not be adequately described by the linear shifts of their individual energy levels.

To anticipate the relative size of the first order term, one can calculate the approximate change in the nuclear charge Z experienced by the radiator electron as it is shielded by plasma electrons. This change can be found by determining the average number of plasma electrons within the radiator electron orbital:

$$\Delta Z = \approx n_e \frac{4\pi \overline{r}}{3} \approx \frac{4\pi n_e a_0^3}{3} \left(\frac{3n_q^2 - l(l+1)}{2Z} \right)^3 . \tag{3.59}$$

From this expression, if we begin with the expression for the bound energy levels and obtain a difference equation, we can obtain an approximate value for $\Delta E^0/E$, due to the first order shift:

$$E = \frac{Z^2}{n_i^2} - \frac{Z^2}{n_f^2}, \tag{3.60}$$

$$\Delta E = \frac{2Z\Delta Z_i}{n_i^2} - \frac{2Z\Delta Z_f}{n_f^2}. \tag{3.61}$$

Using eq. 3.59 and the expressions above, we obtain the following expression:

$$\frac{\Delta E^0}{E} = -\frac{\Delta\lambda^0}{\lambda} \approx -9\pi n_e a_0^3 \left(\frac{n_f^2 n_i^2 [n_f^2 + n_i^2]}{Z^4}\right). \tag{3.62}$$

This rough approximation is provided as an aid to experimentalists. It suggests that the first order shift is strongly dependent on principal quantum number, as well as the ion charge Z. However, the dependence on Z is misleading in the sense that line spectra for low Z ionic radiators are usually broadened beyond recognition before an appreciable shift can be observed.

3.5 Evaluation of $D_{i,i'',i'}(k_1, k_2)$

We will now examine $D_{i,i'',i'}(k_1, k_2)$, which contains second order expression of the the interaction potential, so that we may obtain calculable expressions for $B^{(2)}$ and $M(\omega)$. Employing the Wigner-Eckart theorem, we use eq. 3.37 and the methods introduced in Section 3.3 to insert the expression for a multi-electron matrix element from eq. 3.34 into the expression for $D_{i,i'',i'}(k_1, k_2)$ found in eq. B.14:

$$\begin{aligned}
&k_1^{-2}k_2^{-2}D_{i,i'',i'}(k_1,k_2) \\
&= \sum_{\substack{\alpha,\alpha' \\ \alpha'',\alpha'''}} \sum_{l_1,m_1} \sum_{l_2,m_2} \sum_{t_1,q_1} \sum_{t_2,q_2} (-1)^{q_1-q_2} \langle k_1,l_1,m_1|A_1'^{t_1} C_{-q_1}^{(l_1)}(1)|k_2,l_2,m_2\rangle \\
&\qquad \times \langle k_1,l_1,m_1|A_1'^{t_2} C_{-q_2}^{(t_2)}(1)|k_2,l_2,m_2\rangle^* \\
&\quad \times \mathbf{T}^\dagger_{i,\alpha}(\mathcal{J}) \langle \Psi_{\alpha,\mathcal{J}\mathcal{M}}| \sum_{j=1}^{N_r} A'^{(t_1)}(j) C_{q_1}^{(t_1)}(j) |\Psi_{\alpha'',\mathcal{J}''\mathcal{M}''}\rangle \mathbf{T}_{i'',\alpha''}(\mathcal{J}'') \\
&\quad \times \mathbf{T}^\dagger_{i'',\alpha'''}(\mathcal{J}'') \langle \Psi_{\alpha',\mathcal{J}'\mathcal{M}'}| \sum_{j=1}^{N_r} A'^{(t_1)}(j) C_{q_1}^{(t_1)}(j) |\Psi_{\alpha''',\mathcal{J}''\mathcal{M}''}\rangle^* \mathbf{T}_{i',\alpha'}(\mathcal{J}').
\end{aligned} \tag{3.63}$$

Once again we will have to differentiate between cases where the matrix element is between states of the same configuration and those that are not. We will attempt to simplify the angular portions as we did for $B^{(1)}$, but we must proceed carefully. For example, the ordering of the matrix indices is important, and the angular momenta for state α' needs to maintain the same relationship with α''' as state α has with α'', so indices may seem to be reversed, but it is correct. Since we will reverse the order of the second matrix element, we must remember to take the complex conjugate of the factors. This will be seen mostly in the powers of -1, where $(-1)^K$ will simply be replaced by $(-1)^{-K}$. The 3-j, 6-j, and 9-j symbols are real valued, so we only need to be concerned with having the correct ordering.

We will first obtain the reduced matrix elements of the perturbing electron states,

$$\begin{aligned}
&\sum_{l_1,m_1}\sum_{l_2,m_2}\sum_{t_1,q_1}\sum_{t_2,q_2}(-1)^{q_1-q_2}\langle k_1,l_1,m_1|A_1'^{t_1}C^{(t_1)}_{-q_1}(1)|k_2,l_2,m_2\rangle \\
&\qquad\times\langle k_1,l_1,m_1|A_1'^{t_2}C^{(t_2)}_{-q_2}(1)|k_2,l_2,m_2\rangle^* \\
&= \sum_{l_1,m_1}\sum_{l_2,m_2}\sum_{t_1,q_1}\sum_{t_2,q_2}\langle k_1,l_1||A_1'^{t_1}C^{(t_1)}_1||k_2,l_2\rangle\langle k_1,l_1||A_1'^{t_2}C^{(t_2)}_1||k_2,l_2\rangle^* \\
&\qquad\times(-1)^{l_1-m_1+q_1-l_1+m_1-q_2}\begin{pmatrix} l_1 & t_1 & l_2 \\ -m_1 & -q_1 & m_2\end{pmatrix}\begin{pmatrix} l_1 & t_2 & l_2 \\ -m_1 & -q_2 & m_2\end{pmatrix} \qquad (3.64)
\end{aligned}$$

The advantage of this ordering is that we can employ the sum rule, eq. A.6, by summing over m_1 and m_2 without reordering the expression.

$$\sum_{m_1m_2}(-1)^{q_1-q_2}\begin{pmatrix} l_1 & t_1 & l_2 \\ -m_1 & -q_1 & m_2\end{pmatrix}\begin{pmatrix} l_1 & t_2 & l_2 \\ -m_1 & -q_2 & m_2\end{pmatrix} = \delta_{t_1t_2}\delta_{q_1q_2}\frac{1}{[t_1]} \qquad (3.65)$$

We now know that $t_1 = t_2$ and $q_1 = q_2$. We may now apply the Wigner-Eckart Theorem to the matrix elements of the radiator states,

$$\langle \Psi_{\alpha,\mathcal{J}\mathcal{M}} | \sum_{j=1}^{N_r} A'^{(t_1)}(j) C_{q_1}^{(t_1)}(j) | \Psi_{\alpha'',\mathcal{J}''\mathcal{M}''} \rangle \langle \Psi_{\alpha',\mathcal{J}'\mathcal{M}'} | \sum_{j=1}^{N_r} A'^{(t_1)}(j) C_{q_1}^{(t_1)}(j) | \Psi_{\alpha''',\mathcal{J}''\mathcal{M}''} \rangle^*$$

$$= (-1)^{\mathcal{J}-\mathcal{M}-\mathcal{J}'+\mathcal{M}'} \begin{pmatrix} \mathcal{J} & t & \mathcal{J}'' \\ -\mathcal{M} & q & \mathcal{M}'' \end{pmatrix} \begin{pmatrix} \mathcal{J}' & t & \mathcal{J}'' \\ -\mathcal{M}' & q & \mathcal{M}'' \end{pmatrix}$$

$$\langle \Psi_{\alpha,\mathcal{J}} || \sum_{j=1}^{N_r} A'^{(t_1)}(j) C^{(t_1)}(j) || \Psi_{\alpha'',\mathcal{J}''} \rangle \langle \Psi_{\alpha',\mathcal{J}'} || \sum_{j'=1}^{N_r} A'^{(t)}(j') C^{(t)}(j') || \Psi_{\alpha''',\mathcal{J}''} \rangle^*. \quad (3.66)$$

Once again we can simplify eq. 3.66 by summing over q and $\mathcal{M}''$ using eq. A.7. This is possible because we are summing over states i'' and since $\mathcal{M}''$ is a good quantum number of state i''. Also, both the reduced matrix elements and the transition matrices are invariant in $\mathcal{M}''$. We will refer to the sum over i'' with a prime to indicate that we have summed over $\mathcal{M}''$. Referring to eq. 3.66, we arrive at the following:

$$\sum_{q} \sum_{\mathcal{M}''} (-1)^{\mathcal{J}-\mathcal{J}'+\mathcal{M}-\mathcal{M}'} \begin{pmatrix} \mathcal{J} & t & \mathcal{J}'' \\ -\mathcal{M} & q & \mathcal{M}'' \end{pmatrix} \begin{pmatrix} \mathcal{J}' & t & \mathcal{J}'' \\ -\mathcal{M}' & q & \mathcal{M}'' \end{pmatrix} = \delta_{\mathcal{J}\mathcal{J}'} \delta_{\mathcal{M}\mathcal{M}'} [\mathcal{J}]^{-1}, \quad (3.67)$$

which leaves us with the following expression:

$$
\begin{aligned}
&\sum_{i''} k_1^{-2} k_2^{-2} D_{i,i'',i'}(k_1,k_2) \\
&= \delta_{\mathcal{J}\mathcal{J}'}\delta_{\mathcal{M}\mathcal{M}'} \sum_{i''}{}' \sum_{\substack{\alpha,\alpha' \\ \alpha'',\alpha'''}} \sum_{l_1,l_2} \sum_{t} [t,\mathcal{J}]^{-1} \langle k_1,l_1||A_1^{\prime t_1} C_1^{(t_1)}||k_2,l_2\rangle \\
&\qquad \times \langle k_1,l_1||A_1^{\prime t_2} C_1^{(t_2)}||k_2,l_2\rangle^* \\
&\qquad \times \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \langle \Psi_{\alpha,\mathcal{J}}|| \sum_{j=1}^{N_r} A'^{(t_1)}(j) C^{(t_1)}(j) ||\Psi_{\alpha'',\mathcal{J}''}\rangle \mathbf{T}_{i'',\alpha''}(\mathcal{J}'') \\
&\qquad \times \mathbf{T}^{\dagger}_{i'',\alpha'''}(\mathcal{J}'') \langle \Psi_{\alpha',\mathcal{J}'}|| \sum_{j'=1}^{N_r} A'^{(t)}(j') C^{(t)}(j') ||\Psi_{\alpha''',\mathcal{J}''}\rangle^* \mathbf{T}_{i'',\alpha'}(\mathcal{J}'). \quad (3.68)
\end{aligned}
$$

We cannot go any further with this expression, unless we make some simplifying approximations. We will attempt to reduce the transformation matrices between the matrix elements of the interaction potential to the identity by summing over the energy eigenstates represented by i''. This would seem simple except that the expressions for $B^{(2)}$ and $M(\omega)$ in eqs. 3.23, 3.29, 3.30, 3.31, and 3.32, are dependent on the quantity $\hbar\omega_{i''}$ Let us make the assumption that the states are degenerate within a given manifold. This is a standard assumption as long as level splitting due to the microfield is small relative to the energy spacing between manifolds as well as small relative to the plasma frequency. This approximation is equivalent to setting $\Delta\omega''$ equal to $\Delta\omega' + \omega_{n''n'}$, where $\omega_{n''n'}$ is the average energy difference between the n''th and n'th manifolds. We will also make the assumption that $\mathbf{T}_{\alpha,i}(\mathcal{J})$ is block diagonal in the sense that the cross terms of $\mathbf{T}_{\alpha,i}(\mathcal{J})$ between states of differing manifolds should be negligible. This is reasonable since the basis states are determined by the atomic physics code in such a way that the states of differing manifolds are orthogonal regardless of the angular momentum representation [54].

This allows us to substitute $\hbar\omega_{i''}$ with $\hbar\omega_{i'} + \hbar\omega_{n''n'}$, which commutes with the block-diagonal transformation matrices. We sum $\mathbf{T}_{\alpha'',i''}(\mathcal{J}'')\mathbf{T}^{\dagger}_{i'',\alpha'''}(\mathcal{J}'')$ over i'' to obtain $\delta_{\alpha''\alpha'''}$. We now rewrite $D_{i,i'',i'}(k_1,k_2)$ with just two transformation matrices bracketing the reduced matrix elements. We may now take advantage of the sum over α''.

$$\begin{aligned}
&\sum_{i''} k_1^{-2}k_2^{-2}D_{i,i'',i'}(k_1,k_2) \\
&= \delta_{\mathcal{J}\mathcal{J}'}\delta_{\mathcal{M}\mathcal{M}'}\sum_{\alpha,\alpha'}\sum\alpha''\sum_{l_1,l_2}\sum_{t}[t,\mathcal{J}]^{-1}\langle k_1,l_1||A_1'^{(t)}C_1^{(t)}||k_2,l_2\rangle \\
&\quad\times\langle k_1,l_1||A_1'^{t}C_1^{(t)}||k_2,l_2\rangle^{*}\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J})\langle\Psi_{\alpha,\mathcal{J}}||\sum_{j=1}^{N_r}A'^{(t)}(j)C^{(t)}(j)||\Psi_{\alpha'',\mathcal{J}''}\rangle \\
&\quad\times\langle\Psi_{\alpha',\mathcal{J}}||\sum_{j'=1}^{N_r}A'^{(t)}(j')C^{(t)}(j')||\Psi_{\alpha'',\mathcal{J}''}\rangle^{*}\mathbf{T}_{i',\alpha'}(\mathcal{J}')
\end{aligned} \tag{3.69}$$

As we now evaluate the angular portions of the matrix elements, we will proceed carefully, considering several cases. This problem is described in detail in Appendix E. For a multi-electron atom with no more than two electrons having the same principal quantum number and no interactions between states of differing principal quantum number, we arrive at the following solution when states α, α', and α'' are in the same configuration. The sum over the states α'' that are in the same configuration as the two other states is indicated by a prime.

$$\begin{aligned}
&\sum_{\alpha''}{}'\sum_{s=1}^{q}\sum_{r=1}^{q}\langle\Psi_{\alpha,\mathcal{J}}||w_sA'^{(t)}(s)C^{(t)}(s)||\Psi_{\alpha'',\mathcal{J}''}\rangle\langle\Psi_{\alpha',\mathcal{J}}||w_rA'^{(t)}(r)C^{(t)}(r)||\Psi_{\alpha'',\mathcal{J}''}\rangle^{*} \\
&\quad=\delta_{\alpha\alpha''}\delta_{\alpha'\alpha''}\sum_{r=1}^{q}\frac{[\mathcal{J}_q]}{[l_r]}|\left(w_rA'^{(t)}_{n_rl_rn_rl_r}\langle l_r||C^{(t)}||l_r\rangle\right)^2 \\
&+2\sum_{s=1}^{q}\sum_{r=s+1}^{q}\frac{(-1)^{l_s+l_r}[\mathcal{J}_q]}{[l_r,l_s]^{1/2}}D'(s,r)w_rw_sA'^{(t)}_{n_sl_sn_sl_s}A'^{(t)}_{n_rl_rn_rl_r}\langle l_s||C^{(t)}||l_s\rangle\langle l_r||C^{(t)}||l_r\rangle
\end{aligned} \tag{3.70}$$

This expression is diagonal for the multi-electron cases considered and is similar to the diagonal term of $B^{(1)}$ in the sense that we sum over the contributions from each subshell. Although this expression appears rather formidable, it is analogous to the Law of Cosines; refer to eqs. E.18 and E.20. If one considers the monopole term of the multipole expansion, $t = 0$, $D'(s,r)$ reduces to $(-1)^{l_s+l_r}$ and the equation above can be expressed as a square of the sums. We arrive at the following solution for the second case involving transitioning matrix elements from eq. E.70.

$$\sum_{\alpha''} D \cdot D = \delta_{\alpha\alpha'} \sum_{\text{config}''} (n \cdot k) \frac{[\mathcal{J}]}{[l_\alpha]} \tag{3.71}$$

where the sum is executed over all configurations, except the configuration of state α, as opposed to individual states with differing intermediate angular momentum sums. This simplifies the problem tremendously. The quantity l_α is the orbital angular momentum of the electron undergoing the transition while it is in state α, and n is the occupation number of the subshell containing the transitioning electron in state α and k is the occupation number of the subshell containing the transitioning electron in α''. The matrix elements of all electrons not undergoing transitions reduce to delta functions, and we need only to sum over the angular momentum of the electron undergoing the transition in state α''. We now express $D_{i,i'',i'}(k_1,k_2)$ in terms of Coulomb wavefunctions [57], and express the reduced matrix elements $\langle l||C^{(t)}||l'\rangle$ in terms of 3-j symbols. The following expression is the sum of three terms. The first two are obtained summing over the states α'' which are in the same configuration as states α and α', while the third term is

obtained by summing over all other states α''.

$$
\begin{aligned}
\sum_{i''} D_{i,i''i'}(k_1,k_2) &= D_{i,i'}(k_1,k_2) \\
&= \delta_{\alpha\alpha'} \sum_{\alpha} \sum_{l_1,l_2} \sum_{t} \frac{4}{\pi^2} \sum_{r=1}^{q} w_r^2 \frac{[l_1,l_2,l_r]}{[t]} \begin{pmatrix} l_1 & t & l_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_r & t & l_r \\ 0 & 0 & 0 \end{pmatrix}^2 \\
&\quad \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \left[\int_0^{\lambda_D} dx_1 F_{l_1}(\eta_1,k_1x_1) A^{(t)}_{n_r l_r}(x_1) F_{l_2}(\eta_2,k_2x_1) \right]^2 \mathbf{T}_{i',\alpha}(\mathcal{J}) \\
&+ \delta_{\alpha\alpha'} \sum_{\alpha} \sum_{l_1,l_2} \sum_{t} \frac{8}{\pi^2} \sum_{s=1}^{q} \sum_{r=s+1}^{q} (w_r w_s) \frac{[l_1,l_2][l_r,l_s]^{1/2}}{[t]} \\
&\quad D'(s,r) \begin{pmatrix} l_1 & t & l_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_r & t & l_r \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_s & t & l_s \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \left[\int_0^{\lambda_D} dx_1 F_{l_1}(\eta_1,k_1x_1) A^{(t)}_{n_s l_s}(x_1) F_{l_2}(\eta_2,k_2x_1) \right] \\
&\quad \left[\int_0^{\lambda_D} dx_2 F_{l_2}(\eta_2,k_2x_2) A^{(t)}_{n_r l_r}(x_2) F_{l_1}(\eta_1,k_1x_2) \right] \mathbf{T}_{i',\alpha}(\mathcal{J}) \\
&+ \delta_{\alpha\alpha'} \sum_{\alpha} \sum_{\text{config}''} \sum_{l_1,l_2} \sum_{t} \frac{4}{\pi^2} (n \cdot k) \frac{[l_1,l_2,l_{\alpha''}]}{[t]} \begin{pmatrix} l_i & t & l_j \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_1 & t & l_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \\
&\quad \mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) \left[\int_0^{\lambda_D} dx_1 F_{l_1}(\eta_1,k_1x_1) A^{(t)}_{n_i i n_j l_j}(x_1) F_{l_2}(\eta_2,k_2x_1) \right]^2 \mathbf{T}_{i',\alpha}(\mathcal{J}) \qquad (3.72)
\end{aligned}
$$

We have now obtained the factor $D_{i,i'}(k_1,k_2)$ which contains all the information regarding the second order expression of the radiator-perturbing electron interaction, which is used in $B^{(2)}$ and the real and imaginary parts of $M(\omega)$. It is diagonal for the multi-electron cases under consideration. It is useful for He-like and Li-like satellites of K-shell spectra as well as Li-like and Be-like L-shell spectra. It has

been reduced to a sum over configurations with special consideration for the term when the matrix elements act between the same configuration. For a hydrogenic radiator, n and k and w_r reduce to one and there is no sum over subshell, thereby eliminating the second term. Therefore, eq. 3.72 reduces to the result obtained by Woltz [13, 14].

CHAPTER 4
RESULTS

In this section, we will discuss the results of our calculations using the full-Coulomb, multi-electron formalism. We will show that significant line shifts and asymmetries are revealed by employing the full-Coulomb expression of the radiator-perturbing electron interaction potential. Also, we will compare our results with other models such as a multi-electron formalism employing the dipole approximation and a semi-classical model that contains all orders in the radiator-perturbing electron interaction potential. Finally, we will address the impact the line shift on line merging, especially the importance of including interactions between states of differing principal quantum number, the so-called "mixing" terms.

4.1 Computational Aspects

In order to obtain computed lineshapes, a great deal of information concerning the relativistic atomic physics of the radiator must be obtained. The existing multi-electron line shape code MERL [15, 16] uses as input, energy levels and reduced matrix elements of dipole and quadrupole interactions generated by the suite of atomic physics codes written by Robert Cowan at Los Alamos National Laboratory. In addition, the author of this manuscript also extracted relativistic, multi-electron radial wavefunctions for the bound electron states as well as mixing

coefficients between the LS representation and energy eigenbasis. These coefficients form the basis of our transformation matrices, $\mathbf{T}_{i,\alpha}(\mathcal{J})$.

The reduced dipole matrix elements obtained from the atomic physics had previously been used to calculate the electron broadening operator and are still employed to obtain the radiator-ion microfield interaction. These dipole values, $\langle \alpha || r || \alpha' \rangle$, should not be confused with the the dipole terms in the multipole expansion of the radiator-perturbing electron interaction, which account for the possibility of the plasma electron penetrating the radiator orbital. The radial wavefunctions are written out by the code as a set of functions for each occupied subshell, with the intention of using them as product wavefunctions. The Coulomb wavefunctions are obtained using the Numerov method to solve the appropriate differential equation.

4.2 Shifts and Asymmetries

In this section, we will present the results of our calculations, focusing on the first order shift $B^{(1)}$. From Eqn. 3.17, we know that $B^{(1)}$ is linear in density and is also dependent on temperature, principal quantum number n and orbital angular momentum l. In Figure 4.1 we see the first order shift, $B^{(1)}$, as a function of temperature for Ar+16 immersed in a plasma (any kind, it is not dependent on concentration) characterized by an electron density, $N_e = 1 \times 10^{24} \mathrm{cm}^{-3}$. In the subsections that follow, we consider various factors governing the nature of the calculated shift.

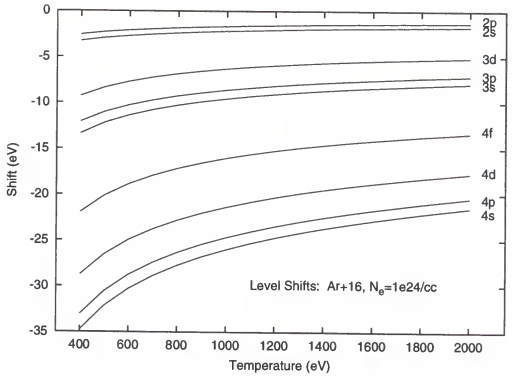


Figure 4.1: Comparison of level shifts, first order in the interaction potential, of Helium-like Ar as a function of temperature; electron density, $1 \times 10^{24}\,\mathrm{cm}^{-3}$. Note the increase in the magnitude of the level shifts with increasing principal quantum number and dependence on angular momentum state.

4.2.1 Dependence on principal quantum number, n

It is apparent from Figure 4.1 that the shift is strongly dependent on the initial states of the radiator, particularly the principal quantum number, n. In physical terms, this can be understood by remembering that a higher shell presents more volume to be penetrated by plasma electrons. Also, for a given principal quantum number, subshells with lower angular momentum have a greater volume, which explains why the s orbital experiences the greatest shift. These results are consistent with the difficulty experienced measuring the shift of lines originating from more tightly bound levels, such as the α- or β-lines, where the calculated shift can be less than the instrumental resolution. The plasma spectroscopy group at University of Florida first noticed an experimentally measurable shift of a He-γ line of Ar+16; it was this observation that subsequently inspired this study. Another benefit of the strong shift dependence on the principal quantum number is the ability to measure differential shifts between members of a Rydberg series. In the measurements that we will discuss, time-resolved x-ray spectrometers were not absolutely calibrated, and the author has had to rely on evaluating the shift of one line relative to another.

4.2.2 Dependence on electron density, n_e

As we stated earlier, the shift and the width are linear in electron density. As a result, the profiles both shift and broaden with increasing electron density. The β- and γ-lines in Figure 4.2 are calculated using the full-Coulomb expression of the radiator-perturbing electron interaction. The dipole approximation is used for the same lines in Figure 4.3.

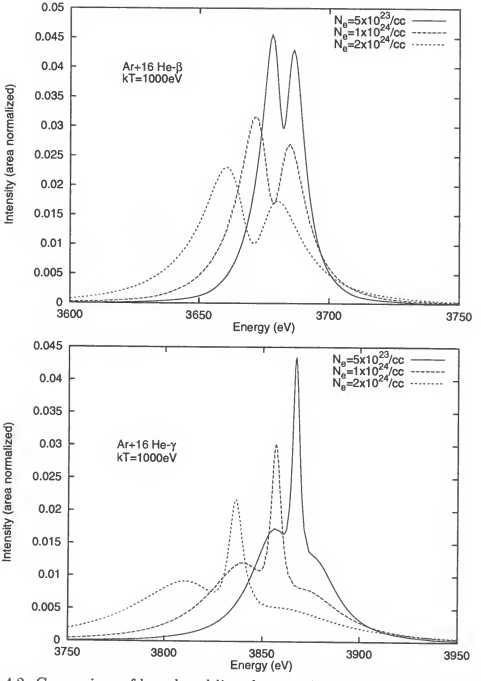


Figure 4.2: Comparison of broadened line-shapes using a full-Coulomb expression for the radiator-perturbing electron interaction. a) The Ar+16 He-β is shown as a function of density, with a temperature, $kT = 1000$ eV. The increasing density causes both broadening and shifting of the lines; b) The Ar+16 He-γ line is shown for the same plasma conditions as a).

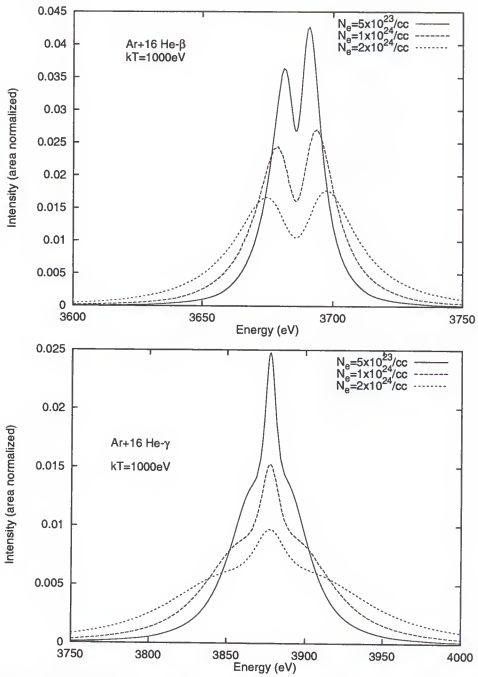


Figure 4.3: Line-shapes of He-like Ar calculated in the dipole approximation of the radiator-perturbing electron interaction, are shown as a function of electron density, with a temperature $kT = 1000$ eV. There are no shifts and the lineshapes appear broader than those shown in Figure 4.4 for the same densities . a) The Ar+16 He-β is shown; b) The Ar+16 He-γ is shown.

The effect of shifts increasing with both increasing electron density and principal quantum number can cause theoretical difficulties when calculating lines in a Rydberg series. One can anticipate, at sufficiently high electron densities, that higher lying lines will shift past their lower n neighbors: of course this result is based on the shift having a linear density dependence. However, since the magnitudes of non-zero, off-diagonal matrix elements of the first-order shift, $B^{(1)}$, are on the order of diagonal elements, we must consider the mixing of adjacent level when making our shift calculations. For example, the matrix element, $B^{(1)}_{4p,5p}$, is about half that of $B^{(1)}_{4p,4p}$. Preliminary calculations have shown that mixing between states within a Rydberg series, due to interactions with perturbing electrons and ions, removes the possibility of higher spectral line passing lower series members. Rather the series members tend to 'pile up' against one another as the plasma density increases. This phenomenon will be addressed in subsequent sections.

4.2.3 Dependence on temperature, kT

Also, from Figure 4.1, one can see the shift is weakly dependent on the plasma temperature. This has led some to use an "ion-sphere" or "uniform electron" model to calculate the shift, which assumes a uniform distribution of electrons within the ion sphere as a high temperature limit [19, 36]. However,in Figure 4.4, we see line asymmetries which become more pronounced as the temperature decreases. Figure 4.4 shows line profiles of the He-β and He-γ of Ar+16 as a function of temperature for $N_e = 1 \times 10^{24}\text{cm}^{-3}$. The shifted profile shapes are more strongly dependent on temperature than line profiles calculated in the dipole approximation, as seen in Figure 4.5.

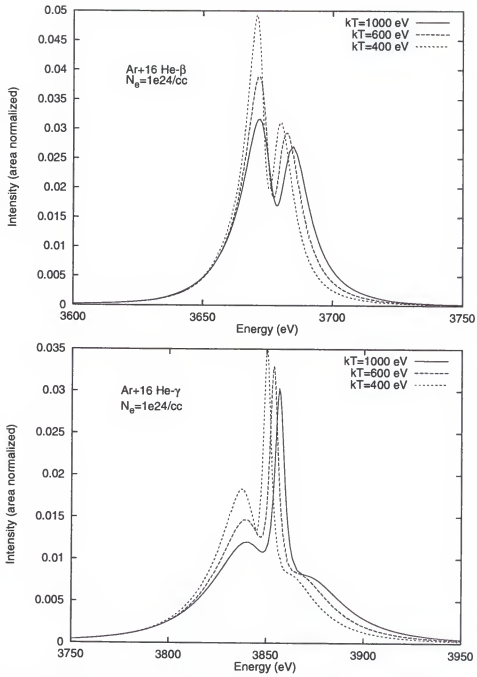


Figure 4.4: Comparison of broadened line-shapes using a full-Coulomb expression for the radiator-perturbing electron interaction. a) The Ar+16 He-β is shown as a function of temperature, with an electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. The shift in the full-Coulomb calculation causes increasing asymmetry as the temperature decreases; b) The Ar+16 He-γ line is shown for the same plasma conditions as a).

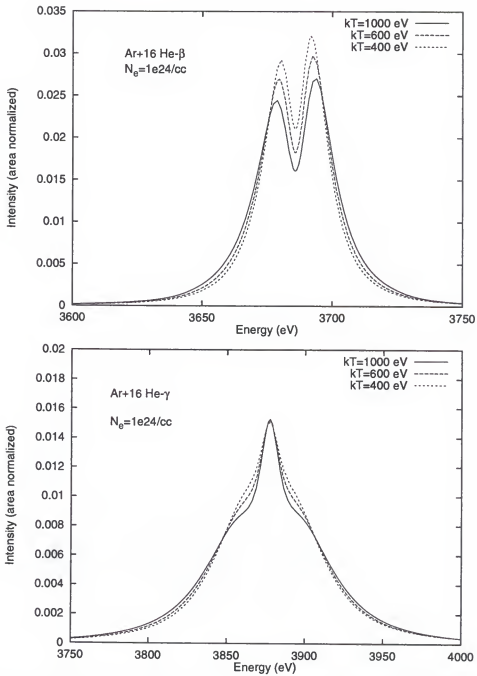


Figure 4.5: Line-shapes of He-like Ar calculated in the dipole approximation of the radiator-perturbing electron interaction, are shown as a function of temperature, with an electron density, $N_e = 1 \times 10^{24} \mathrm{cm}^{-3}$. There are no shifts or asymmetries in the line-shapes, and the temperature dependence is not as pronounced as is seen in Figure 4.4. a) The Ar+16 He-β is shown; b) The Ar+16 He-γ is shown.

4.2.4 Dependence on orbital angular momentum, l

The differing shifts of the angular momentum states observed in Figure 4.1 can result in a distinct asymmetry of the line profile. The calculated line-shape asymmetries arise from the splitting of angular momentum states, due primarily to the interaction with the ion microfield. The β- and γ-lines in Figure 4.4 represent the $1s3p - 1s^2$ and $1s4p - 1s^2$ transitions, respectively; however, the p states are mixed with other angular momentum states by Stark splitting of the line. Each Stark component shifts differently according to its constituent angular momentum states. However, sum rules regarding the dipole oscillator strength must still be obeyed. As a result, the centers of mass of the line profiles in Figure 4.4 shift at the rate of the $1snp - 1s^2$ transition, but the "peaks" shift less, reflecting the mixing with the higher angular momentum states.

4.2.5 Dependence on ion charge, Z

Finally, the shift is very weakly dependent on the radiator ion charge Z. The shift increases with decreasing ion charge; in other words, a β-line from Helium-like Ar will shift slightly more than the the Ly-β of Ar. This property justifies comparing shifts between members of the same Rydberg series as opposed to attempting to observe a shift between lines from the same transition but differing ionization stages. For example, observing the Ar He-β line and its Li-like satellites has been a useful diagnostic of temperature and density in laser implosion experiments; however, the complex of lines all shift approximately the same amount. Therefore, since absolute calibration of spectral data was not available, a bulk shift of the line complex might be interpreted as calibration error.

4.3 Comparison with Other Models

In this section, we will compare our results with those based on other models. We find that the first order shift that we calculate compares well with two sets of calculations based on impact models that include the effects of the monopole term of the radiator-perturbing electron interaction. Also, we compare our results with a semi-classical, all-order model and find good agreement within the regions of the validity of the second order approximation. In Figure 4.6, the current model is compared with calculations by Griem *et al.* [23] and Nguyen*et al.* [24]. Griem *et al.* used a distorted wave method to determine the phase shift of perturbing electron due to the penetrating monopole interaction with the radiator. Since they employed a Born approximation, theirs is a first order result and agrees very well with the first order result of the current model. Nguyen *et al.* used a quantum mechanical impact model similar to the current model.

In the electron-density and temperature regime under consideration, the second order theoretical results were corroborated by independent calculations using an all-order, semi-classical model [58, 59]. Figure 4.7 shows Lyman-β and Lyman-γ profiles at a typical temperature, 1000 eV and electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$, which corresponds to plasma conditions observed in ICF experiments. Ones sees good agreement between the two models, although the second order calculation has a slightly larger shift. Figure 4.8 shows Lyman-β and Lyman-γ lines at a lower temperature, 600 eV, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. Even here the models have not yet begun to diverge significantly. However, we can notice minor differences in the shifts and the width is slightly greater in the second order calculation. Finally, we compare calculations of the Ly-β line at kT=300eV in Figure 4.9 in Figure 4.9. Here we

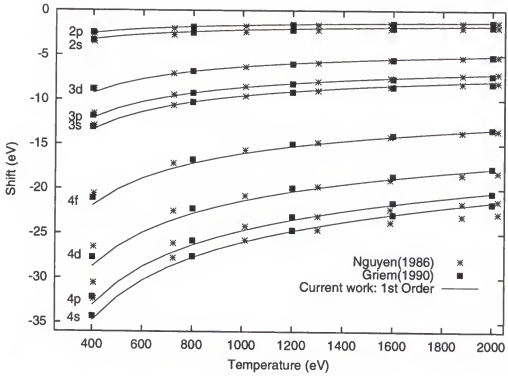


Figure 4.6: Comparison of shifts, first order in the interaction potential, of Helium-like Ar with a shift calculations by Griem *et al.* (1990) and Nguyen *et al.* (1986); electron density, $1 \times 10^{24}\,\mathrm{cm}^{-3}$. There is excellent agreement with Griem and good agreement with Nguyen.

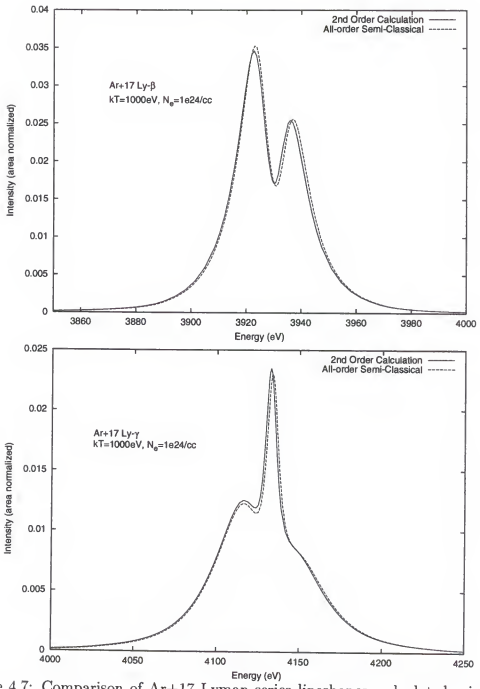


Figure 4.7: Comparison of Ar+17 Lyman series lineshapes, calculated using the second-order, quantum mechanical formalism and an all-order, semi-classical expression, for a temperature 1000 eV and an electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. Notice that there is very good agreement. a) The Ar+17 Ly-β is shown; b) The Ar+17 Ly-γ is shown.

begin to see differences between the two models. According to the conditions set forth by Cooper, Kelleher, and Lee [30], the temperature limit for a second order calculation would be and 460 eV and 260 eV for the Lyman β- and γ-lines of Ar+17, respectively, indicating that the apparent difference is consistent with this validity condition. As was stated earlier, this may confirm that strong collisions have become more important at lower temperatures. A strong collision is defined as one where momentum transfer is large with respect to the initial momentum of the colliding electron. It may seem counter-intuitive that penetrating electrons can undergo weak collisions but one must realize that the momentum transfer is dependent on the duration of the collision as well as on the proximity of the perturber. Thus, sufficiently fast electrons can still experience weak collisions. We expect that the second order approximation will be valid under the conditions specified by CKL [30]. It is unlikely that one can observe β or γ lines of K-shell Argon at temperatures below 600 eV, but they might be observed in absorption.

Although the second order approximation is sufficient for isolated lines of highly ionized radiators under most conditions where such lines would be observed, there are imaginable cases where the second order approximation is not valid. It has been stated that the second order approximation breaks down for frequency separations from line center that are much greater than the plasma frequency. Lines emitted from low-Z radiators, such as HeII, can have widths much larger than the plasma frequency. This condition also occurs when attempting to calculate adjacent lines in a Rydberg series simultaneously. Such a calculation is necessary when studying line merging. We will discuss such calculations in a later section under conditions where they may seem inappropriate; however we must remember that the plasma

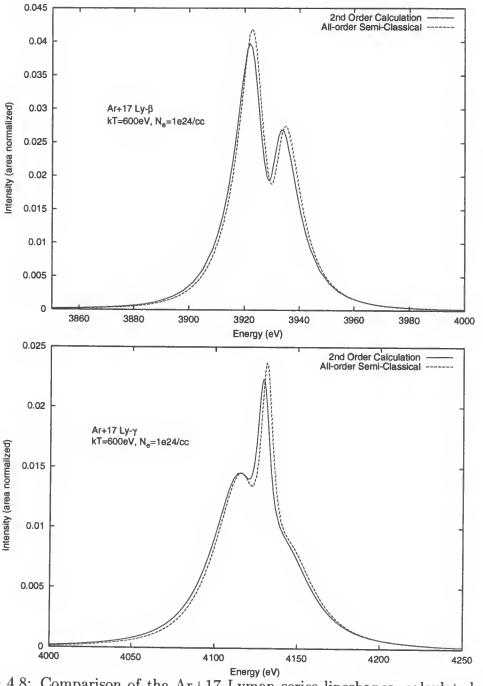


Figure 4.8: Comparison of the Ar+17 Lyman series lineshapes, calculated using the second-order, quantum mechanical formalism and an all-order, semi-classical expression, for a temperature 600 eV and an electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. As the temperature decreases there is still good agreement, but they do begin to diverge. a) The Ar+17 Ly-β is shown; b) The Ar+17 Ly-γ is shown.

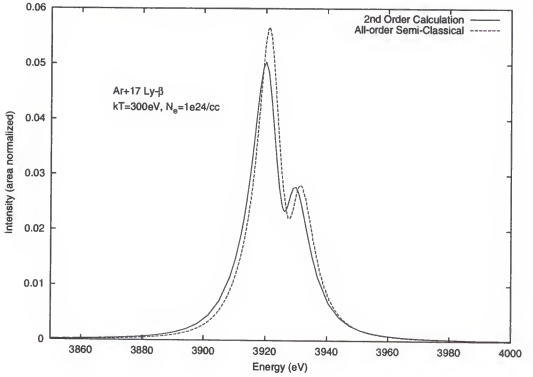


Figure 4.9: Comparison of the Ar+17 Ly-β lineshape, calculated using the second-order, quantum mechanical formalism and an all-order, semi-classical expression, for a temperature 300 eV and an electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. We now begin to see significant differences.

frequency increases with electron density and our model may still be appropriate at these ultra-high densities.

4.4 Experimental Analysis

Using theoretical line-shapes which include shifts, significant improvements have been achieved in interpreting experimental data. Time-resolved Ar K-shell (3-4.5keV) spectra were obtained during microballoon implosions performed using the OMEGA laser system at the Laboratory for Laser Energetics at the University of Rochester [60]. 20 micron thick CH microballoons of 440 micron inner radius were filled with 20 Atm of DD doped with 0.25% Ar. The microballoons were imploded by 20-25 kJ of ultraviolet energy distributed symmetrically among 60 beams. Time-resolved Ar x-ray line spectra provide signatures of plasma conditions during the implosion. The spectra were recorded using a streaked spectrograph with a RbAP crystal dispersing the spectrum onto a 250 Angstrom Au photocathode. Spectral- and temporal resolution were approximately $E/\Delta E \approx 500$ and $\Delta t \approx 20 - 30$ps, respectively. The resulting images were recorded on film, then digitized. Verifying the presence of shifts first requires careful determination of isolated-ion line position, the digitized images were corrected for film sensitivity and known streak camera induced distortions including streak angle and curvature of iso-temporal lines [61]. The dispersion relation was determined by the line positions at early time, when the low densities assured negligible shifts. This same dispersion relation was then used for all times. The theoretical line positions were those obtained using Cowan's [54] atomic physics suite as input into our spectral line profile calculation. Figure 4.10 shows time resolved spectra for a single implo-

sion where the isolated ion line positions have been indicated with vertical lines. The line shifts of the γ-lines are clearly visible.

Before making comparisons with experimental data, the theoretical spectrum was modified to account for 1) shell opacity, 2) streak-camera filtering, 3) Au photocathode response, and 4) the instrumental response function due mainly to source size broadening. No arbitrary, wholesale shift of the theoretical spectrum or individual lines was permitted. In order to analyze the data, theoretical spectra were calculated using the following lines: Ar He-β ($1s3l \rightarrow 1s^2$), He-γ, He-δ, Ly-β, Ly-γ, Ly-δ and the attendant satellites of the He-β, He-γ, and Ly-β. It is important to include satellites since their appearance in the spectra can be incorrectly interpreted as broadening and shifting of the resonance lines. Also included were the effects of ion dynamics, ion-quadrupole interactions, Doppler-, opacity-, and instrumental broadening.

In order to save computer time, theoretical lineshapes were calculated in the dipole approximation for the electron width, with the first order shift included in the calculation. This approximation, when compared with our more exact calculations, has been shown to be adequate for data analysis under the conditions specified. This method works for two reasons. First, it has been shown that using the dipole approximation for the radiator-perturbing electron interaction gives a good approximation for the width even for cases where the inter-electron spacing is comparable with the average bound electron radius.[13, 14] Secondly, we have found that the first order term of the electron shift $B^{(1)}$ provides the dominant contribution to the shift. In Figures 4.11 and 4.12 we show a comparison, respectively, of the Ar+17 Ly-β and Ly-γ, -δ and -ϵ lines, calculated with the

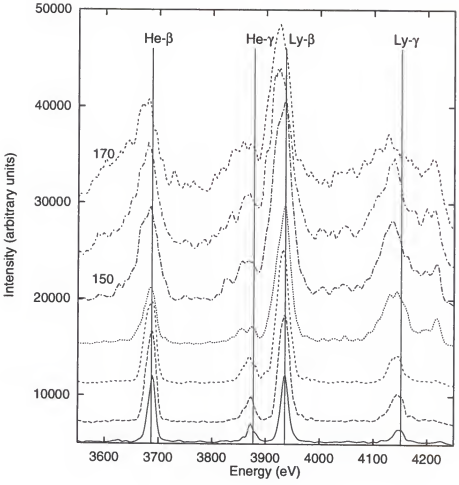


Figure 4.10: Time-resolved lineouts from LLE shot 10778 (.125% Ar in D_2). Vertical lines represent isolated ion line positions of, going from left to right, Ar He-β, He-γ, Ly-β, and Ly-γ. Note how the γ lines shift more than the β lines. Time progresses in the upward direction.

full-Coulomb model of the electron shift and width operator with interactions between the upper manifolds, and a profile calculated in the dipole approximation for the electron width with a first order shift included, but no interactions between the upper manifolds. We can see that with a typical resolution and for a high plasma density, the full-Coulomb calculation of the Ly-β line produces a slightly narrower profile than does the dipole approximation; also it has a little greater shift. At these electron densities, the β-line can be satisfactorily approximated by the dipole approximation with the first order shift. However, even though the γ-line experiences a great deal of interaction with the δ and ϵ lines, causing it to be broader than it would appear in an isolated calculation, the dipole calculation provides a noticeably different profile: the contrast of peak height to wing intensity is substantially greater.

We have shown lines for He-like radiators, but not for more complex lineshapes, which are used in the analysis of K-shell Ar spectra. Figure 4.13 compares the Ar^{+16} He-β and its Li-like, $n = 2$ satellite calculated in the full-Coulomb formalism with lineshapes calculated in the dipole approximation. We can see that the lineshapes of the satellites have little structure, particularly with respect to the primary resonance line. It has been known that the dipole calculation provides a good approximation for the width. While here it may be possible to shift the entire lineshape calculated in the dipole approximation by an amount equal to the first order shift, for lineshapes with more structure it may be necessary to include the detailed, angular momentum-dependent shift into the initial calculation, so that the asymmetries apparent.

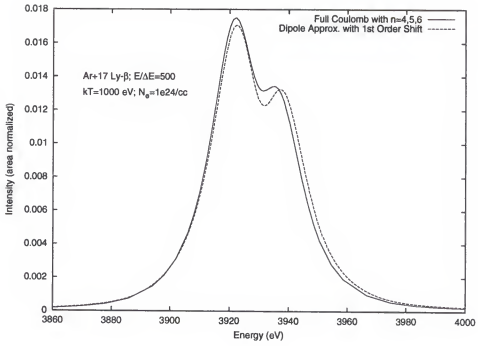


Figure 4.11: This figure compares the Ly-β of 1% Ar^{+17} in D_2, where the effects due to plasma electrons are calculated in the dipole approximation, with a first order, linear shift included, and with a full-Coulomb expression of the radiator-plasma electron interaction potential, with interactions between the n=3,4,5 and 6 manifolds. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$. The profiles were convolved with a Gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$.

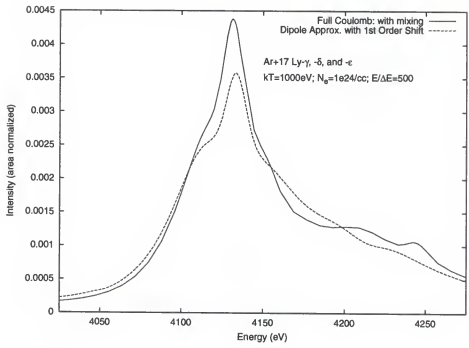


Figure 4.12: This figure compares the Ly-γ through -ϵ of 1% Ar^{+17} in D_2, where the effects due to plasma electrons are calculated in the dipole approximation, with a first order, linear shift included, and with a full-Coulomb expression of the radiator-plasma electron interaction potential, with interactions between the n=3,4,5 and 6 manifolds. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$. The profiles were convolved with a gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$.

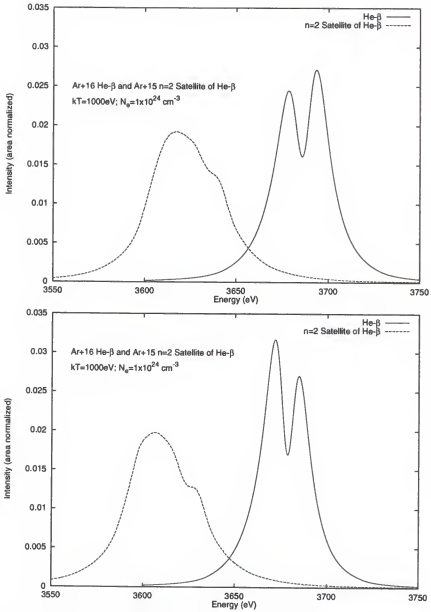


Figure 4.13: This figure compares the Ar^{+16} Li-like, $n = 2$ satellite of the He-β. The temperature, kT=1000eV and electron density, $N_e = 1 \times 10^{24}\text{cm}^{-3}$. a) These lines were calculated in the dipole approximation; b) The full-Coulomb expression of the radiator-perturbing electron interaction was used. One can see there is little difference in the width of the satellite lines.

In Figure 4.14, spectroscopic data, lineout 170 from Omega shot 10778, is shown together with the 'best fit' unshifted- and shifted-theoretical profiles, where only temperature and density are adjustable parameters. A model spectrum characterized by the temperature $kT = 1250$ eV and electron density $N_e = 1.5 \times 10^{24}\text{cm}^{-3}$ was found to be the best fit to the data. It should be noted that because the α, β, and γ lines shift by significantly different amounts, one cannot shift the theoretical spectrum by an arbitrary amount and fit the entire spectrum. In particular, the region containing the Ar He-γ and Ly-β lines provides an excellent test of any theory of shifts, as experimental uncertainties are unlikely to vary appreciably over this 200 eV spectral range. Figure 4.14 illustrates the size of the shift relative to the widths and demonstrate a good agreement of theory to experiment when the shifts are included. Also, time resolved data from Nova shot 26031209 is shown in Figure 4.15, while in Figure 4.16lineout e from Nova shot 26031209 is shown together with the 'best fit' unshifted- and shifted-theoretical profiles for a temperature of $kT = 1000$ eV and electron density $N_e = 6 \times 10^{23}\text{cm}^{-3}$. Notice how the shifted Ly-β line picks up the asymmetry of the spectral data.

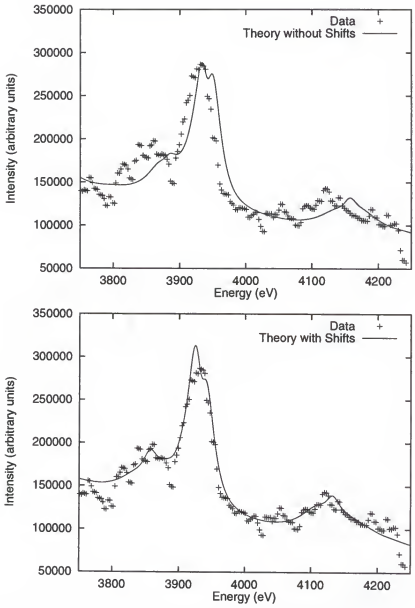


Figure 4.14: Detail from lineout 170 from shot 10778 (.125% Ar in D_2) and fits using model spectrum, for $n_e = 1.5 \times 10^{24}\,\mathrm{cm}^{-3}, kT = 1250$ eV. Edge effects on the data due to the photocathode can be seen just to the right of the Lyman-γ line, where the spectrum seems to drop off rapidly. The model spectrum has been convolved with a gaussian with a fwhm of approximately 6-7 eV to account for instrumental broadening. a) Unshifted lineshapes were used for the model spectrum; b) Shifted lineshapes were used for the model spectrum.

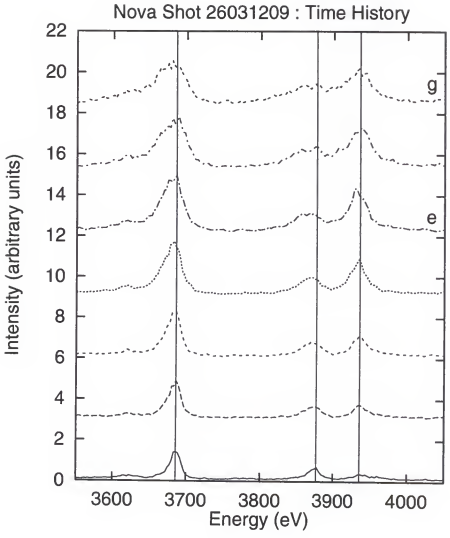


Figure 4.15: Time-resolved lineouts from Nova shot 26031209 (.2% Ar in D_2). Vertical lines represent isolated ion line positions of, going from left to right, Ar He-β, He-γ, Ly-β. Note how the γ lines shift more than the β lines. Time progresses in the upward direction.

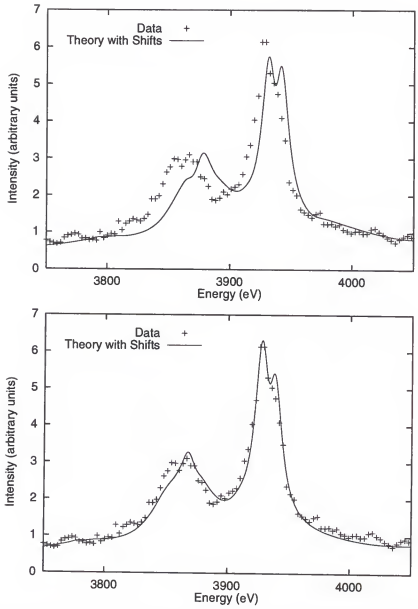


Figure 4.16: Detail from lineout e from shot Nova shot 26031209 (.2% Ar in D_2) and fits of the Ar He-γ and Ly-β using model spectrum, for $n_e = 6 \times 10^{23}$ cm^{-3}, $kT =$ 1000 eV. The model spectrum has been convolved with a Gaussian with a fwhm of approximately 6-7 eV to account for instrumental broadening. a) Unshifted lineshapes were used for the model spectrum; b) Shifted lineshapes were used for the model spectrum.

4.5 Line Merging and Continuum Lowering

At very high electron densities, $> 1 \times 10^{24}$/cc, higher lying series members of Ar+17 experience plasma induced shifts greater than those of more tightly bound lower series members, allowing for the possibility for line to shift past its neighbor. However, as the densities increase, the splitting of adjacent energy levels due to the ion microfield, together with the line shift, allows for the eventual overlap of states, and requires these previously isolated states be treated as composite states. Mathematically, the magnitudes of non-zero matrix elements of the first-order shift, $B^{(1)}$, due to mixing between states of differing principal quantum number, are on the order of diagonal elements. For example, the element, $B^{(1)}_{4p,5p}$, is about half that of $B^{(1)}_{4p,4p}$. We will show that the inclusion of mixing between states within a Rydberg series produces a non-linear shift theory: this in turn tends to cause the lines to 'pile up' against one another during the line merging process. In order to demonstrate the effects mixing between upper manifolds, we must calculate the lineshapes over very large frequency ranges with respect to the plasma frequency. It has already been stated that the second order calculation's validity fails for frequency separations greater than two times the plasma frequency. Therefore, one must understand that these results offer only a qualitative understanding of line merging; however, at some point the levels become sufficiently close to allow the accurate calculation of spectral line originating from these composite states. In Figure 4.17, we show the Lyman series of Ar^{+17} from the β-line to the ϵ-line as higher lying series members are successively added to the calculation of the composite line profile; the electron density is increased from $1 \times 10^{24}\text{cm}^{-3}$ to $3 \times 10^{24}\text{cm}^{-3}$ and $5 \times 10^{24}\text{cm}^{-3}$.

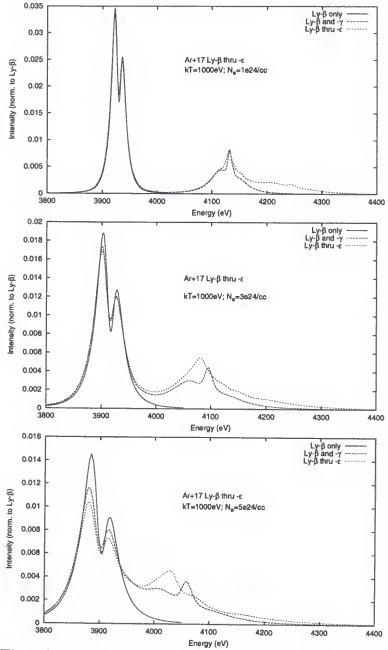


Figure 4.17: These figures compare the Ly-β through -ϵ of 1% Ar^{+17} in D_2, as higher series members are added to the calculation of a composite line shape using the full-Coulomb model and accounting for interactions between states of differing principal quantum number. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, a) $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$; b) $n_e = 3 \times 10^{24}\,\mathrm{cm}^{-3}$; c) $n_e = 5 \times 10^{24}\,\mathrm{cm}^{-3}$.

In Figure 4.18 we show the full-Coulomb calculation of the Ar^{+17}Ly-β through -ϵ with and without interactions between upper manifolds at electron densities, $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$, and $n_e = 5 \times 10^{24}\,\mathrm{cm}^{-3}$. In Figures 4.19 and 4.20 are shown details of the individual lines at a the lower density. The line widths and shifts appear to be reasonably approximated by a linear model at the lower density; however, the peak of the Ly-γ experiences an accelerating shift and an increase in its intensity relative to the Ly-β. Currently, there is not data available at sufficiently high densities to confirm this behavior.

We also show a comparision in Figure 4.21 with the dipole calculation with a first order, linear shift included. Once again, the approximation is adequate for the lower density, but fails dramatically at the higher density. This clearly demonstrates the limitations of the dipole approximation.

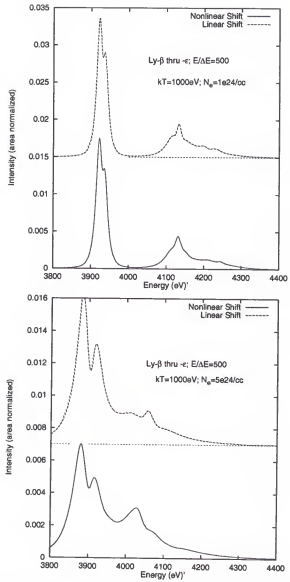


Figure 4.18: These figures compare the Ly-β through -ϵ of 1% Ar^{+17} in D_2, calculated with and without mixing between upper manifolds, the former of which can result in non-linear shifts at sufficiently high densities. The profiles were convolved with a gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, a) $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$; b) $n_e = 5 \times 10^{24}\,\mathrm{cm}^{-3}$; differences are clearly apparent at this resolution for the higher density. The lineshapes calculated with the linear model were displaced vertically by an arbitrary amount for display purposes.

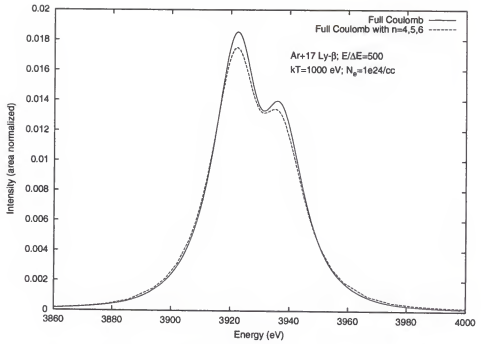


Figure 4.19: This figure compares the Ly-β of 1% Ar^{+17} in D_2, where the effects due to plasma electrons are calculated in the full-Coulomb expression of the radiator-plasma electron interaction potential, with and without interactions between the n=3,4,5 and 6 manifolds. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$. The profiles were convolved with a gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$.

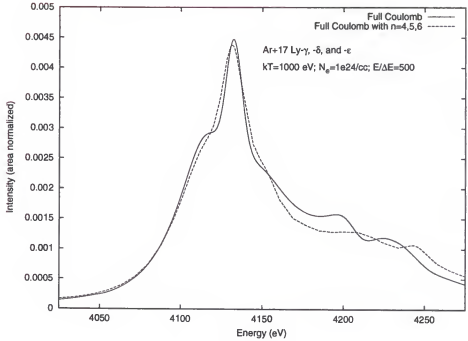


Figure 4.20: This figure compares the Ly-γ through -ϵ of 1% Ar^{+17} in D_2, where the effects due to plasma electrons are calculated in the full-Coulomb expression of the radiator-plasma electron interaction potential, with and without interactions between the n=3,4,5 and 6 manifolds. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$. The profiles were convolved with a gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$.

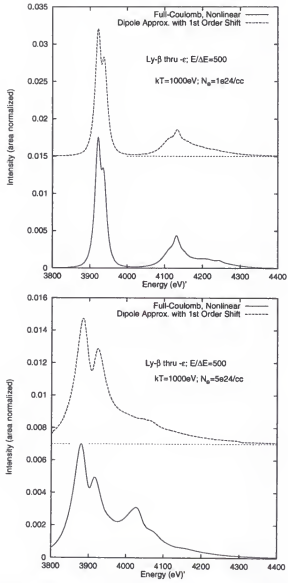


Figure 4.21: These figures compare the Ly-β through -ϵ of 1% Ar^{+17} in D_2, where the effects due to plasma electrons are calculated in the dipole approximation, with a first order, linear shift included, and with a full-Coulomb expression of the radiator-plasma electron interaction potential, with a non-linear shift. The profiles were convolved with a gaussian with fwhm corresponding to an instrumental resolution $E/\Delta E = 500$. The lineshapes were calculated for plasmas characterized by a temperature, kT=1000eV and electron density, a) $n_e = 1 \times 10^{24}\,\mathrm{cm}^{-3}$; b) $n_e = 5 \times 10^{24}\,\mathrm{cm}^{-3}$; it is clear the approximations are no longer valid at the higher density. The lineshapes calculated in the dipole approximation were displaced vertically by an arbitrary amount for display purposes.

CHAPTER 5
CONCLUSION

In this work, we presented a generalized full-Coulomb formalism of line broadening for multi-electron ions, where the line shifts arise consistently from the relaxation theory. We compared our results with other available models and compared model spectra calculated with the line shift with experimental data. Certain simplifying approximations were tested that could save computer time and man-hours spent applying more involved models when it may not be necessary. Finally, we considered the impact of the shift on line merging and proposed that the shift may have a measurable effect on plasma phenomenon dependent on energy level structure.

We discovered that incorporating the dense plasma line shift into line spectra calculations can have a significant effect on the position and overall shape of line profiles from highly ionized, moderate Z radiators.

From a strictly applied point of view this is immediately useful. We found that including the shift in line spectra from highly ionized, moderate Z radiators has improved plasma diagnostics. We have shown the lineshapes with the shift are more temperature sensitive than those calculated in the dipole approximation, which is also an important issue in diagnostics. We then showed that employing the dipole approximation with the first order shift is an acceptable alternative to the full-Coulomb calculation for highly ionized, moderate Z radiators, in cases where the second order approximation is valid and the orbital size is less than or

approximately equal to the inter-electron spacing, particularly for the computer intensive multi-electron calculations. These results are significant because plasma diagnostics may be extended to greater densities as researchers attempt to achieve "break even" in fusion research, as well as being applied to astrophysical studies.

If we consider a wider perspective, we can speculate on the impact that the shifts will have on plasma phenomena dependent on the energy level structure of radiators as they interact with hot, dense plasmas. Now that we demonstrated that including mixing between upper states of differing principal quantum number introduces non-linear behavior of the shift as adjacent members of a Rydberg series merge, we must redefine the distinction between continuum and bound states and among bound states themselves. Ionization balance is sensitive to changes in energy level structure [33, 34, 35, 36, 37], and opacity is sensitive to the energy location of line emission. Therefore, understanding the effect of the shift near the continuum edge is very important. The shift may have a measurable effect on continuum lowering, ionization balance, and opacity calculations, as well as line ratio diagnostics.

There are areas that need further examination. First, as the nuclear charge Z decreases, the first order shift becomes smaller relative to the width. Higher order terms have greater significance. We did not explore this in detail; on the other hand, the observed shifts are small and apparently have little effect on line merging. Second, at this time, we cannot not easily compare our line merging results with those of an all-order calculation, which would be a more appropriate choice for studying adjacent lines. Such a comparison would be quite interesting. Third, other concerns arise as the density increases, the binary-collision assumption and

the effect of plasma electron correlations has been over-simplified, we may need to consider how these matters are treated in condensed matter physics. Fourth, the plasma electrons do not act in isolation, we have commented little about the effects of the plasma ions in conjunction with the electrons. Finally, at this time we do not have experimental evidence to confirm the line-merging behavior predicted by our theory. This is due to our inability to generate sufficiently high plasma densities and temperatures in the laboratory. The few experiments where such densities were observed were focused on the α-lines which would have been unaffected by line merging in that plasma regime [62].

Future experiments are planned in which we expect to observe sufficiently high densities and temperatures, thereby affording us an opportunity to verify our predictions.

APPENDIX A
3N-J SYMBOLS AND IRREDUCIBLE TENSOR OPERATORS

This appendix provides brief overview of a formalism that is very useful for the treatment of angular momentum dependent matrix elements. These definitions, identities, and sum rules will be employed throughout this work. First, we will introduce a Wigner 3N-j symbols [54, 63, 64] in terms of an integral over spherical harmonics,

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{lm} Y_{kq} Y_{l'm'} sin\theta d\theta d\phi = (-1)^m \left(\frac{[l,k,l']}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} l & k & l' \\ -m & q & m' \end{pmatrix} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}, \tag{A.1}$$

where

$$[l,l',\ldots] = (2l+1)(2l'+1)\cdots. \tag{A.2}$$

There are several useful relations and symmetry properties that will be employed in this work, such as

$$\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \tag{A.3}$$

and

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \tag{A.4}$$

The following relation can be obtained using the orthogonality of spherical harmonic functions,

$$\begin{pmatrix} j & j' & 0 \\ m & -m' & 0 \end{pmatrix} = (-1)^{j-m}[j]^{-1/2}\delta_{jj'}\delta_{mm'}. \tag{A.5}$$

Also, the equation $m_1 + m_2 + m_3 = 0$ must be satisfied for a 3-j symbol to be nonzero. Below we state several useful sum rules:

$$\sum_{j_3}\sum_{m_3}[j_3]\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1 m_1'}\delta_{m_2 m_2'}, \tag{A.6}$$

$$\sum_{m_1}\sum_{m_2}[j_3]\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \delta_{j_3 j_3'}\delta_{m_3 m_3'}\delta(j_1 j_2 j_3), \tag{A.7}$$

and,

$$\sum_{m}(-1)^{j-m}\begin{pmatrix} j & j & j_3 \\ m & -m & 0 \end{pmatrix} = \delta_{j_3 0}[j]^{1/2}, \tag{A.8}$$

where $\delta(j_1 j_2 j_3)$ is $+1$ if the triangle relations are satisfied.

Also, we will be making extensive use of the Wigner-Eckart Theorem [55, 56], which is written below. We will employ the theorem to express the matrix elements of our interaction potential in terms of reduced matrix elements, as follows:

$$\langle \alpha j m | T_q^{(k)} | \alpha' j' m' \rangle = (-1)^{j-m}\begin{pmatrix} j & k & j' \\ m & q & -m' \end{pmatrix}\langle \alpha j || T^{(k)} || \alpha' j' \rangle, \tag{A.9}$$

where $T_q^{(k)}$ is an irreducible tensor operator, j and j' are the angular momentum indices of the coordinates relevant to the operator, and α and α' represent all the other quantities (energy, spin, etc.) that define their respective states.

A particular example of reduced matrix elements that will be employed is the matrix elements of spherical harmonics. We will be writing the angular portion of our radiator-perturbing electron interaction in terms of normalized spherical harmonics, defined as,

$$C_q^{(k)}(\theta,\phi) = \left(\frac{4\pi}{[k]}\right)^{1/2} Y_{kq}(\theta,\phi). \tag{A.10}$$

Several relations pertaining to reduced matrix elements of spherical harmonics are written below:

$$\langle l||C^{(k)}||l'\rangle = (-1)^l[l,l']^{1/2}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}, \tag{A.11}$$

$$\langle \alpha l||C^{(0)}||\alpha l'\rangle = [l]^{1/2}\delta_{\alpha,\alpha'}\delta_{l,l'}, \tag{A.12}$$

and

$$\langle l'||C^{(k)}||l\rangle = (-1)^k\langle l||C^{(k)}||l'\rangle. \tag{A.13}$$

We will also use 6-j and 9-j symbols to evaluate the angular portions of multi-electron matrix elements. The symbols are defined as follows:

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{array} \right\} = [j_3] \sum_{m_1 m_2} \sum_{n_1 n_2 n_3} \left(\begin{array}{ccc} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{array} \right) \left(\begin{array}{ccc} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{array} \right) \left(\begin{array}{ccc} l_1 & j_2 & l_3 \\ -n_1 & m_2 & n_3 \end{array} \right) \left(\begin{array}{ccc} l_1 & l_2 & j_3 \\ n_1 & -n_2 & m_3 \end{array} \right), \quad \text{(A.14)}$$

and

$$\left\{ \begin{array}{ccc} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{array} \right\} = \sum_j (-1)^{2j} [j] \left\{ \begin{array}{ccc} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & j \end{array} \right\} \left\{ \begin{array}{ccc} j_{12} & j_{22} & j_{32} \\ j_{21} & j & j_{23} \end{array} \right\} \left\{ \begin{array}{ccc} j_{13} & j_{23} & j_{33} \\ j & j_{11} & j_{12} \end{array} \right\} \text{(A.15)}$$

We will make extensive use of the following relations when one of the arguments is zero as well as orthogonality relations. With regard to symmetry properties, a 6-j symbol is unchanged when any two columns are interchanged, as well as if any two numbers in the bottom row are interchanged with the corresponding two numbers in the top row. The arguments in the top row must satisfy a triangle relation,

$$|l_2 - l_3| \leq l_1 \leq l_2 + l_3, \quad |l_1 - l_3| \leq l_2 \leq l_1 + l_3, \quad |l_1 - l_2| \leq l_3 \leq l_1 + l_2, \text{ (A.16)}$$

and their sum be a non-negative integer. Also, any set of arguments that can be permuted into the top row must also satisfy these conditions.

The orthogonality relation for 6-j symbols can be written as follows:

$$\sum_{l_3}[j_3,l_3]\left\{\begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{array}\right\}\left\{\begin{array}{ccc} j_1 & j_2 & j_3' \\ l_1 & l_2 & l_3 \end{array}\right\} = \delta_{j_3 j_3'}. \tag{A.17}$$

We will also make use of the following sum rule in section E.1 of Appendix E,

$$\sum_{l_3}(-1)^{j_3+l_3+j}[l_3]\left\{\begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{array}\right\}\left\{\begin{array}{ccc} j_1 & l_1 & j \\ j_2 & l_2 & l_3 \end{array}\right\} = \left\{\begin{array}{ccc} j_1 & j_2 & j_3 \\ l_2 & l_1 & j \end{array}\right\}. \tag{A.18}$$

The following relation is employed extensively throughout Appendices D and E, when one of the arguments of a 6-j symbol is zero,

$$\left\{\begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & 0 \end{array}\right\} = \delta_{j_1 j_2 j_3}\delta_{j_1 l_2}\delta_{l_1 j_2}(-1)^{j_1+j_2+j_3}[j_1,j_2]^{-1/2}. \tag{A.19}$$

Returning to 9-j symbols, one must multiply the symbol by a factor of $(-1)^K$, where K is the sum of all the arguments when exchanging a pair of columns or rows. The arguments in any row or column must satisfy a triangle relation and their sum must be a nonnegative integer. The orthogonality relations are written as follows:

$$\sum ik[i,k,s,t]\left\{\begin{array}{ccc} A & B & s \\ C & D & t \\ i & k & E \end{array}\right\}\left\{\begin{array}{ccc} A & B & s' \\ C & D & t' \\ i & k & E \end{array}\right\} = \delta_{ss'}\delta_{tt'} \tag{A.20}$$

$$\sum st[i,k,s,t] \begin{Bmatrix} A & B & s \\ C & D & t \\ i & k & E \end{Bmatrix} \begin{Bmatrix} A & B & s \\ C & D & t \\ i' & k' & E \end{Bmatrix} = \delta_{ii'}\delta_{kk'} \qquad \text{(A.21)}$$

The following relation is used when one of the arguments is zero,

$$\begin{Bmatrix} a & b & e \\ c & d & e \\ f & f & 0 \end{Bmatrix} = (-1)^{b+c+e+f}[e,f]^{-1/2} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}. \qquad \text{(A.22)}$$

APPENDIX B
DETERMINING THE FORM OF $B^{(1)}$, $B^{(2)}$, AND $M(\omega)$

In the following chapter, we will obtain forms of the various terms of the electron shift and width operator in terms of their matrix elements. These terms of the electron shift and width operator have not previously been presented together in a detailed manner, and we intend to show that our results have been obtained in a consistent fashion.

B.1 Matrix Elements of $B^{(1)}$

In the series of steps below, the Liouville operator representing $B^{(1)}$ is expressed as a commutator to get the two terms shown. Complete sets of states are inserted to obtain the correct matrix elements acting on an arbitrary operator dependent on radiator coordinates, $\hat{\Omega}$, as follows,

$$\begin{aligned}
\sum_{\mu'\nu'} B^{(1)}_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} &= n\sum_{\mu'\nu'}[\mathrm{Tr}_1 L_1(r,1)f_0(1)]_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} \\
&= n\sum_{\alpha}[\langle\mu\alpha|V_1(r,1)f_0(1)\hat{\Omega}|\nu\alpha\rangle - \langle\mu\alpha|f_0(1)\hat{\Omega}V_1(r,1)|\nu\alpha\rangle] \\
&= n\sum_{\mu'\alpha\alpha'}[\langle\mu\alpha|V_1(r,1)f_0(1)|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu\alpha\rangle \\
&\quad - \langle\mu\alpha|f_0(1)|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}V_1(r,1)|\nu\alpha\rangle], \\
\sum_{\mu'\nu'} B^{(1)}_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} &= n\sum_{\mu'\nu'\alpha\alpha'\alpha''}[\langle\mu\alpha|V_1(r,1)f_0(1)|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\alpha''\rangle\langle\nu'\alpha''|\nu\alpha\rangle \\
&\quad - \langle\mu\alpha|f_0(1)|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\alpha''\rangle\langle|\nu'\alpha''|V_1(r,1)|\nu\alpha\rangle]. \qquad \text{(B.1)}
\end{aligned}$$

The operator, $\hat{\Omega}$, does not act on perturbing electron states, therefore its matrix elements are diagonal in the perturbing electron states. Also, the distribution function for the perturbing electron states, $f_0(1)$, will be diagonal in both radiator and perturber electron states, so that we may simplify this last expression,

$$\begin{aligned}\sum_{\mu'\nu'} B^{(1)}_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} &= n\sum_{\mu'\nu'\alpha\alpha'\alpha''}[\langle\mu\alpha|V_1(r,1)|\mu'\alpha\rangle f_0(\alpha)\hat{\Omega}_{\mu'\nu'}\delta_{\nu\nu'}\delta_{\alpha'\alpha''}\delta_{\alpha''\alpha} \\ &- f_0(\alpha)\hat{\Omega}_{\mu'\nu'}\langle\nu'\alpha|V_1(r,1)|\nu\alpha\rangle\delta_{\mu\mu'}\delta_{\alpha\alpha'}\delta_{\alpha'\alpha''}]. \qquad \text{(B.2)}\end{aligned}$$

Hence, expression for $B^{(1)}_{\mu\nu\mu'\nu'}$ can be written as,

$$B^{(1)}_{\mu\nu\mu'\nu'} = n\sum_{\alpha} f_0(\alpha)\left[\langle\mu\alpha|V_1(r,1)|\mu'\alpha\rangle\delta_{\nu\nu'} - \langle\nu'\alpha|V_1(r,1)|\nu\alpha\rangle\delta_{\mu\mu'}\right]. \qquad \text{(B.3)}$$

In order to calculate this quantity, we will express the perturbing electron states in terms of a wavenumber, ($\alpha \rightarrow \mathbf{k}$), representing solutions to the eigenvalue problem of free electrons in the presence of an ion. Referring to Eq. 3.4, we define our basis set in terms of $H(1)$,

$$H(1) = \frac{p_1^2}{2m} - \frac{(Z-1)}{x_1}, \qquad \text{(B.4)}$$

$$H(1)|\mathbf{k}\rangle = \frac{k^2\hbar^2}{2m}|\mathbf{k}\rangle. \qquad \text{(B.5)}$$

We then express the sum over α as an integral over $\mathbf{k}$, and arrive at the following expression for $B^{(1)}$,

$$B^{(1)} = n\int d\mathbf{k} f(k)\left[\langle\mu;\mathbf{k}|V_1(r,1)|\mu';\mathbf{k}\rangle\delta_{\nu\nu'} - O.T.\right], \qquad \text{(B.6)}$$

where the other term ($O.T.$) includes matrix elements between statesν and ν'. We shall make the assumption that the plasma electrons are in local thermal equilibrium and employ a Maxwellian distribution for $f_0(1)$, so that

$$f_0(1) = \lambda_T^3 e^{-\frac{\beta k^2 \hbar^2}{2m}}, \quad \text{where} \quad \lambda_T = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{\frac{1}{2}}. \tag{B.7}$$

We substitute these expressions into eq. B.6 to obtain the following:

$$B^{(1)} = n\lambda_T^3 \int d\mathbf{k} e^{-\frac{\beta k^2 \hbar^2}{2m}} \left[\langle \mu; \mathbf{k}|V_1(r,1)|\mu'; \mathbf{k}\rangle \delta_{\nu\nu'} - O.T.\right], \tag{B.8}$$

so that equation B.8 will be a starting point to evaluate $B^{(1)}$ in section 3.4.

B.2 Matrix Elements of $B^{(2)}$

We will follow a similar method as was used in section B.1 to obtain $B^{(2)}$ in terms of matrix elements of $V_1(r,1)$. We therefore return to eq. 3.18,

$$B^{(2)} = -n\mathrm{Tr}_1 \left[L_1(r,1) f_0(r) f_0(1) \int_0^\beta d\tau e^{\tau[H(r)+H(1)]} V_1 e^{-\tau[H(r)+H(1)]} f_0(r)^{-1} \right]. \tag{B.9}$$

Using the same notation as in section B.1, we re-express $L_1(r,1)$ as a commutator, we get the following expression:

$$\sum_{\mu'\nu'} B^{(2)}_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} = -n\sum_{\alpha}\int_0^\beta d\tau\langle\mu\alpha|V_1(r,1)f_0(r)f_0(1)e^{\tau[H(r)+H(1)]} \times V_s(r,1)e^{-\tau[H(r)+H(1)]}f_0(r)^{-1}\hat{\Omega}|\nu\alpha\rangle + n\sum_{\alpha}\int_0^\beta d\tau\langle\mu\alpha|f_0(r)f_0(1)e^{\tau[H(r)+H(1)]}V_s(r,1)e^{-\tau[H(r)+H(1)]} \times f_0(r)^{-1}\hat{\Omega}V_1(r,1)|\nu\alpha\rangle. \quad \text{(B.10)}$$

Next, as we did for $B^{(1)}$, we will insert complete sets of radiator and perturber states and express $B^{(2)}$ in terms of the matrix elements of the interaction $V_1(r,1)$, so that we can execute the integral over τ,

$$B^{(2)}_{\mu\nu\mu'\nu'} = -n\sum_{\mu''}\sum_{\alpha\alpha'}\int_0^\beta d\tau\langle\mu\alpha|V_1(r,1)|\mu''\alpha'\rangle f_0(\mu'')f_0(\alpha')e^{\tau[\omega_{\mu''}+\omega_{\alpha'}]} \times\langle\mu''\alpha'|V_s(r,1)|\mu'\alpha\rangle e^{-\tau[\omega_{\mu'}+\omega_\alpha]}f_0(\mu')^{-1}\delta_{\nu\nu'} + n\sum_{\alpha\alpha'}\int_0^\beta d\tau f_0(\mu)f_0(\alpha)e^{\tau[\omega_\mu+\omega_\alpha]}\langle\mu\alpha|V_s(r,1)|\mu'\alpha'\rangle \times e^{-\tau[\omega_{\mu'}+\omega_{\alpha'}]}f_0(\mu')^{-1}\langle\nu'\alpha'|V_1(r,1)|\nu\alpha\rangle. \quad \text{(B.11)}$$

Once again, express the perturber states α and α' in terms of the wave-numbers $\mathbf{k}_1$ and $\mathbf{k}_2$ respectively, and substitute the sums over α and α' with integrals,

$$B^{(2)}_{\mu\nu\mu'\nu'} = -n\int d\mathbf{k}_1\int d\mathbf{k}_2\sum_{\mu''}\langle\mu\mathbf{k}_1|V_1(r,1)|\mu''\mathbf{k}_2\rangle\langle\mu''\mathbf{k}_2|V_s(r,1)|\mu'\mathbf{k}_1\rangle \times f_0(\mu'')f_0(k_2)f_0(\mu')^{-1}\int_0^\beta d\tau e^{\tau[\omega_{\mu''}+\frac{k_2^2\hbar^2}{2m}-\omega_{\mu'}-\frac{k_2^2\hbar^2}{2m}]}\delta_{\nu\nu'} + O.T. \quad \text{(B.12)}$$

We now execute the integral over τ to obtain the following expression:

$$B^{(2)}_{\mu\nu\mu'\nu'} = -n\int d\mathbf{k}_1 \int d\mathbf{k}_2 \sum_{\mu''} \langle \mu \mathbf{k}_1 | V_1(r,1) | \mu'' \mathbf{k}_2 \rangle \langle \mu'' \mathbf{k}_2 | V_s(r,1) | \mu' \mathbf{k}_1 \rangle f_0(\mu'') \times f_0(k_2) f_0(\mu')^{-1} \frac{\left(\exp\{\beta[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m} - \frac{k_1^2\hbar^2}{2m}]\} - 1 \right)}{[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m} - \frac{k_1^2\hbar^2}{2m}]} \delta_{\nu\nu'} + O.T. \qquad \text{(B.13)}$$

In order to simplify eq. B.13, we define the expression, $D_{\mu\mu''\mu'}(k_1, k_2)$, which contains all the information concerning the second order radiator-perturbing electron interaction. We also express the perturber states in terms of a partial wave expansion where l and m describe the angular momentum state, and k is the wave number, so that we arrive at the following expression:

$$D_{\mu,\mu'',\mu'}(k_1,k_2) = k_1^2 k_2^2 \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} \langle \mu k_1, l_1, m_1 | V_s(r,1) | \mu'' k_2, l_2, m_2 \rangle \langle \mu'' k_2, l_2, m_2 | V_s(r,1) | \mu' k_1, l_1, m_1 \rangle. \qquad \text{(B.14)}$$

We will now substitute Boltzmann distributions for $f_0(\mu')$, $f_0(\mu'')$ and $f_0(k_2)$ and then substitute $D_{\mu\mu''\mu'}(k_1, k_2)$ into eq. B.13,

$$B^{(2)}_{\mu\nu\mu'\nu'} = -\delta_{\nu\nu'} n \lambda_T^3 \int dk_1 \int dk_2 \sum_{\mu''} D_{\mu\mu''\mu'}(k_1,k_2) \frac{\left(e^{-\beta[\frac{k_2^2\hbar^2}{2m}]} - e^{-\beta[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m}]} \right)}{\left[\omega_{\mu''} - \omega_{\mu'} + \frac{k_2^2\hbar^2}{2m} - \frac{k_1^2\hbar^2}{2m} \right]} + O.T., \qquad \text{(B.15)}$$

where the other term ($O.T.$) contains the matrix elements between ν and ν' as well as μ and μ', which is often called an interference term.

The expression $D_{\mu\mu''\mu'}(\mathbf{k}_1, \mathbf{k}_2)$ is common to both $B^{(2)}$ and $M(\omega)$ and will prove to be the most challenging portion to simplify and evaluate. We now proceed to finding an expression for $M(\omega)$ in terms of matrix elements of $V_1(r, 1)$.

B.3 Matrix Elements of $M(\omega)$

Returning to eq. 3.8, we see that $M(\omega)$ is already at least second order in the radiator-perturbing electron potential $\mathcal{L}(r, 1)$. We should replace $[\omega - L(r) - L(1)]^{-1}$ for $[L(r) + L(1) + \mathcal{L}(r, 1)]^{-1}$ in order to keep the interaction to second order. Instead, we will replace $\mathcal{L}(r, 1)$ with $\langle L_1(r, 1)\rangle$, or $B^{(1)}$. This is necessary because the first order shift can be too large to treat perturbatively. We therefore obtain the following expression

$$M(\omega) = n\mathrm{Tr}_1\{\mathcal{L}(r,1)[\omega - L(r) - L(1) - B^{(1)}]^{-1} f(r1)\mathcal{L}(r,1)f(r)^{-1}\}, \qquad \text{(B.16)}$$

which can be expressed as a Laplace transform,

$$M(\omega) = -in\mathrm{Tr}_1\left\{\mathcal{L}(r,1)\int_0^\infty dt\, e^{i(\omega - L(r) - L(1) - B^{(1)} + i\epsilon_+)t} f(r1)\mathcal{L}(r,1)f(r)^{-1}\right\}. \qquad \text{(B.17)}$$

Now we will expand out the Liouville operators in terms of commutators in the next four equations:

$$\sum_{\mu'\nu'} M(\omega)_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} = \lim_{\epsilon\to 0^+} -in\int dt\, e^{i(\omega + i\epsilon_+)t}$$
$$\sum_\alpha \langle \mu\alpha|\mathcal{L}(r,1)e^{-i(L(r)+L(1)+B^{(1)})t} f(r1)\mathcal{L}(r,1)f(r)^{-1}\hat{\Omega}|\nu\alpha\rangle, \qquad \text{(B.18)}$$

which leads to the following expression as one commutator is expanded,

$$\begin{aligned}\sum_{\mu'\nu'} M(\omega)_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} = -in\int dt\, e^{i(\omega+i\epsilon_+)t} \\ \sum_{\alpha}\langle\mu\alpha|\mathcal{L}(r,1)e^{-i(L(r)+L(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}\hat{\Omega}|\nu\alpha\rangle \\ - \langle\mu\alpha|\mathcal{L}(r,1)e^{-i(L(r)+L(1)+B^{(1)})}f(r1)f(r)^{-1}\hat{\Omega}V_s(r,1)|\nu\alpha\rangle. \qquad \text{(B.19)}\end{aligned}$$

We now expand the time development operators as well as the other Liouville operators to arrive at the following:

$$\begin{aligned}\sum_{\mu'\nu'} M(\omega)_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} = \lim_{\epsilon\to 0^+} -in\int dt\, e^{i(\omega+i\epsilon_+)t}\sum_{\alpha} \\ \langle\mu\alpha|V_s(r,1)e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}\hat{\Omega}e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle \\ - \langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}\hat{\Omega}e^{i(H(r)+H(1)+B^{(1)})t}V_s(r,1)|\nu\alpha\rangle \\ - \langle\mu\alpha|V_s(r,1)e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}\hat{\Omega}V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle \\ + \langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}\hat{\Omega}V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}V_s(r,1)|\nu\alpha\rangle. \\ \qquad \text{(B.20)}\end{aligned}$$

In the next steps, we will introduce complete sets of states to obtain an expression for $M(\omega)$ in terms of matrix elements of $V_s(r,1)$:

$$\sum_{\mu'\nu'} M(\omega)_{\mu\nu\mu'\nu'}\hat{\Omega}_{\mu'\nu'} = \lim_{\epsilon\to 0^+} -in\int dt\, e^{i(\omega+i\epsilon_+)t}\sum_{\mu'\nu'}\sum_{\alpha\alpha'\beta'}\{$$

$$\langle\mu\alpha|V_s(r,1)e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\beta'\rangle$$

$$\langle\nu'\beta'|e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle$$

$$-\ \langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\beta'\rangle$$

$$\langle\nu'\beta'|e^{i(H(r)+H(1)+B^{(1)})t}V_s(r,1)|\nu\alpha\rangle$$

$$-\ \langle\mu\alpha|V_s(r,1)e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\beta'\rangle$$

$$\langle\nu'\beta'|V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle$$

$$+\ \langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}|\mu'\alpha'\rangle\langle\mu'\alpha'|\hat{\Omega}|\nu'\beta'\rangle$$

$$\langle\nu'\beta'|V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}V_s(r,1)|\nu\alpha\rangle\Big\}, \qquad \text{(B.21)}$$

We will now add another set of states to the first and last terms to obtain

$$M(\omega)_{\mu\nu\mu'\nu'} = \lim_{\epsilon\to 0^+} -in\int dt\, e^{i(\omega+i\epsilon_+)t}\sum_{\alpha\alpha'}$$

$$\sum_{\mu''\alpha''}\langle\mu\alpha|V_s(r,1)|\mu''\alpha''\rangle\langle\mu''\alpha''|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}|\mu'\alpha'\rangle$$

$$\langle\nu'\alpha'|e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle$$

$$-\langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)V_s(r,1)f(r)^{-1}|\mu'\alpha'\rangle\langle\nu'\alpha'|e^{i(H(r)+H(1)+B^{(1)})t}V_s(r,1)|\nu\alpha\rangle$$

$$-\langle\mu\alpha|V_s(r,1)e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}|\mu'\alpha'\rangle\langle\nu'\alpha'|V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}|\nu\alpha\rangle$$

$$+\ \sum_{\nu''\alpha''}\langle\mu\alpha|e^{-i(H(r)+H(1)+B^{(1)})t}f(r1)f(r)^{-1}|\mu'\alpha'\rangle$$

$$\langle\nu'\alpha'|V_s(r,1)e^{i(H(r)+H(1)+B^{(1)})t}|\nu''\alpha''\rangle\langle\nu''\alpha''|V_s(r,1)|\nu\alpha\rangle. \qquad \text{(B.22)}$$

We will assume $H(r)$, $H(1)$, and $B^{(1)}$, along with the corresponding distribution functions, are diagonal in the radiator and perturber states. With some simplifying and renaming of indices in the next few sets of equations, we obtain the following expression:

$$
\begin{aligned}
M(\omega)_{\mu\nu\mu'\nu'} \;=\; & \lim_{\epsilon\to 0^+} -in \int dt\, e^{i(\omega+i\epsilon_+)t} \sum_{\alpha\alpha'} \\
& \{\sum_{\mu''} \langle\mu\alpha|V_s(r,1)|\mu''\alpha'\rangle\langle\mu''\alpha'|V_s(r,1)|\mu'\alpha\rangle f(\mu''\alpha')f(\mu')^{-1} \\
& \qquad e^{i(E_{\nu'}-E_{\mu''}+E_\alpha-E_{\alpha'}+B^{(1)}_{\nu'}-B^{(1)}_{\mu''})t}\delta_{\nu'\nu} \\
& - \langle\mu\alpha|V_s(r,1)|\mu'\alpha'\rangle\langle\nu'\alpha'|V_s(r,1)|\nu\alpha\rangle f(\mu\alpha)f(\mu')^{-1} \\
& \qquad e^{i(E_{\nu'}-E_\mu+E_{\alpha'}-E_\alpha+B^{(1)}_{\nu'}-B^{(1)}_\mu)t} \\
& - \langle\mu\alpha|V_s(r,1)|\mu'\alpha'\rangle\langle\nu'\alpha'|V_s(r,1)|\nu\alpha\rangle f(\mu'\alpha')f(\mu')^{-1} \\
& \qquad e^{i(E_\nu-E_{\mu'}+E_\alpha-E_{\alpha'}+B^{(1)}_\nu-B^{(1)}_{\mu'})t} \\
& + \sum_{\nu''\alpha'} \langle\nu'\alpha|V_s(r,1)|\nu''\alpha'\rangle\langle\nu''\alpha'|V_s(r,1)|\nu\alpha\rangle f(\mu\alpha)f(\mu)^{-1} \\
& \qquad e^{i(E_{\nu''}-E_\mu+E_{\alpha'}-E_\alpha+B^{(1)}_{\nu''}-B^{(1)}_\mu)t}\delta_{\mu,\mu'}. \qquad \text{(B.23)}
\end{aligned}
$$

The first and last terms represent the second order shift and width operators from upper and lower states, respectively. The middle terms are interference terms. The calculational details will be similar, so we will focus on the first term. We will express the perturbing electron states in terms of the partial wave expansion and re-express the matrix elements of the interaction potential in terms of the expression for $D_{\mu\mu'}(\mathbf{k}_1,\mathbf{k}_2)$ in Eq. B.14, where $\Delta\omega_{\mu'\nu} = \omega - E_{\mu'} + E_\nu$, Finally, we employ the Boltzmann distribution functions to obtain final our expression for

$M(\omega)$ as follows,

$$M(\omega)_{\mu\nu\mu'\nu'} = \delta_{\nu'\nu} \lim_{\epsilon\to 0^+} -in\lambda_t^3 \int dk_1 \int dk_2 D_{\mu\mu'}(k_1,k_2) e^{-\beta[\frac{k_2^2\hbar^2}{2m}]} \int dt\, e^{i(\Delta\omega_{\mu'\nu} + \frac{k_1^2\hbar^2}{2m} - \frac{k_2^2\hbar^2}{2m} + B_\nu^{(1)} - B_{\mu'}^{(1)} + i\epsilon_+)t}. \tag{B.24}$$

APPENDIX C
GENERAL TRANSITION ARRAYS

In this appendix, we shall describe in more detail the functions of operators D_1 through D_7 shown in Equations 3.40 and 3.41. More information can be found in Section 14-11 of Cowan's book *The Theory of Atomic Structure and Spectra*, 1981.[54] First, we must introduce the labeling of angular momentum states in the geneological $\mathcal{LS}$ basis with the following notation:

$$\{[(l_1^{w_1}\alpha_1 L_1 S_1, l_2^{w_2}\alpha_2 L_2 S_2)\mathcal{L}_2\mathcal{S}_2, l_3^{w_3}\alpha_3 L_3 S_3]\mathcal{L}_3\mathcal{S}_3, \ldots\}\mathcal{L}_q\mathcal{S}_q\mathcal{J}_q\mathcal{M}_q, \tag{C.1}$$

where l_m is the orbital angular momentum of a single electron in the subshell m, w_m is the occupation number of that subshell, α_m represents all other quantum numbers of that subshell, and q is the total number of relevant subshells. L_m is the sum of orbital angular momentum of all the electrons within subshell m, with the corresponding value for spins S_m. The intermediate sum of the total angular momentum up to and including subshell m is $\mathcal{L}_q$, with a corresponding value for spin. Finally, the quantum numbers representing the total angular momentum, which couples $\mathcal{L}_q$ and $\mathcal{S}_q$, are $\mathcal{J}_q$ and $\mathcal{M}_q$.

Most of the factors described in this appendix are derived when coupled angular momentum states are uncoupled in order to evaluate the matrix element of a single angular momentum coordinate. We often will be applying the identities found in

eqs. 11.38 and 11.39 in Cowan, and they are written below,

$$\langle \alpha_1 j_1 \alpha_2 j_2 j || T^{(k)}(1) || \alpha_1' j_1' \alpha_2' j_2' j' \rangle$$
$$= \delta_{\alpha_2 j_2, \alpha_2' j_2'} (-1)^{j_1 + j_2 + j' + k} [j, j']^{1/2} \begin{Bmatrix} j_1 & j_2 & j \\ j' & k & j_1' \end{Bmatrix} \langle \alpha_1 j_1 || T^{(k)}(1) || \alpha_1' j_1' \rangle \quad \text{(C.2)}$$

$$\langle \alpha_1 j_1 \alpha_2 j_2 j || W^{(k)}(2) || \alpha_1' j_1' \alpha_2' j_2' j' \rangle$$
$$= \delta_{\alpha_1 j_1, \alpha_1' j_1'} (-1)^{j_1 + j_2' + j + k} [j, j']^{1/2} \begin{Bmatrix} j_1 & j_2 & j \\ k & j' & j_2' \end{Bmatrix} \langle \alpha_2 j_2 || W^{(k)}(2) || \alpha_2' j_2' \rangle, \quad \text{(C.3)}$$

where $T^{(k)}(1)$ and $W^{(k)}(2)$ are irreducible tensor operators acting on differing coordinates of a coupled angular momentum state. The indices j_1 and j_1' represent the angular momentum states of the first coordinate, with similar notation for the second set. The total angular momentum is represented by j and j'. All other quantum numbers of the coordinates are represented by α_1 and α_2. These expressions will be employed throughout Appendices D and E. A brief explanation of 6-j symbols can be found in Appendix A.

In calculating a general transition array, we assume that it is a one-electron transition, in other words, an electron moves from one occupied subshell in the first state to another subshell in the final state, while all other electrons remain in the same subshells during the transition. We employ the convention that an electron moves from a "lower" subshell to a "higher" subshell. We can find the reverse transition by evaluating the complex conjugate of the matrix element.

$$\langle \Psi_j | \hat{\mathbf{V}} | \Psi_i \rangle = \left(\langle \Psi_i | \hat{\mathbf{V}} | \Psi_j \rangle \right)^* . \quad \text{(C.4)}$$

We must introduce some notation that will be used to describe a "general transition." A one electron transition can be described in its most general sense as follows:

$$l_1^{w_1} \cdots l_i^n \cdots l_j^{k-1} \cdots l_q^{w_q} \rightarrow l_1^{w_1} \cdots l_i^{n-1} \cdots l_j^k \cdots l_q^{w_q}, \tag{C.5}$$

where l_m represents the orbital angular momentum of an electron occupying the mth subshell, w_m is the occupation number of the m subshell, q is the total number of relevant subshells. If one were considering a hydrogenic atom, $n = k = 1$, and all other occupation numbers would equal zero. This notation will be used throughout Appendices D and E.

The factor D_1 arises from coordinate permutations as well as addressing cases where the occupancy of a relevant subshell is greater than one. This term is analogous to $\sum_{s=1}^{q} w_s \cdots$ for matrix elements between states with the same configuration,

$$D_1 = (-1)^{\Delta p}(n \cdot k)^{1/2}, \tag{C.6}$$

where

$$\Delta p = k - 1 + \sum_{m=i+1}^{j-1} w_m, \tag{C.7}$$

The factor D_2 arises from coefficient of fractional parentage expansions when the transition involves subshell occupied by more than two electrons. Coefficients of fractional parentage arise when the angular momentum of a transitioning electron is uncoupled from the angular momenta of the other electrons occupying the same subshell as the transitioning electron. For the case when only one or zero electrons shares a subshell with the transitioning electron, the sum of the remaining angular

momenta is trivial, so such a factor reduces to one.

$$D_2 = (l_i^n \alpha_i L_i \mathrm{S}_i \{| l_i^{n-1} \alpha_i' L_i' \mathrm{S}_i')(l_j^{k-1} \alpha_j L_j \mathrm{S}_j \{| l_j^k \alpha_j' L_j' \mathrm{S}_j'), \tag{C.8}$$

where the notation above is defined and described in more detail in section 9.5 in Cowan. The particular examples we will explore will have no more than two electrons in the relevant subshells i and j.

The factor D_3 arises from the uncoupling of the total spin $\mathcal{S}_q$ and the total orbital angular momentum $\mathcal{L}_q$ from the total angular momentum ${\mathcal{J}'}_q$, using eq. C.2,

$$D_3 = \delta_{\mathcal{S}_q,\mathcal{S}_q'}(-1)^{\mathcal{L}_q+\mathcal{S}_q+{\mathcal{J}'}_q+t}[{\mathcal{J}'}_q,\mathcal{J}_q]^{1/2} \begin{Bmatrix} \mathcal{L}_q & \mathcal{S}_q & \mathcal{J}_q \\ \mathcal{J}_q' & t & \mathcal{L}_q' \end{Bmatrix}. \tag{C.9}$$

This expression will be applied to cases where the matrix elements act between states with the same configuration and those that do not.

The factor D_4 is a product of terms arising from the successive uncoupling of orbital angular momenta for subshells included following the subshells relevant to the transition,

$$D_4 = \prod_{m=j+1}^{q} \delta_{\alpha_m L_m \mathrm{S}_m, \alpha_m' L_m' \mathrm{S}_m'} \delta_{\mathcal{S}_m,\mathcal{S}_m'} (-1)^{\mathcal{L}_{m-1}+L_m+\mathcal{L}_m'+t} \times[\mathcal{L}_m,\mathcal{L}_m']^{1/2} \begin{Bmatrix} \mathcal{L}_{m-1} & L_m & \mathcal{L}_m \\ \mathcal{L}_m' & t & \mathcal{L}_{m-1}' \end{Bmatrix}. \tag{C.10}$$

Like D_3, this is applied to cases where the matrix elements act between states with the same configuration and also between those that do not have the same configuration.

The factor D_5 arises from recoupling the angular momenta and spin of the lower subshell relevant to the transition L_i with the intermediate total orbital angular momentum, including the next lower subshell, $\mathcal{L}_{i-1}$ after the last electron coordinate has been uncoupled,

$$D_5 = \left(\prod_{m=1}^{i-1} \delta_{\alpha_m L_m S_m, \alpha'_m L'_m S'_m} \delta_{\mathcal{L}_m S_m, \mathcal{L}'_m S'_m}\right) (-1)^{\mathcal{L}_{i-1}+L'_i+l_i+\mathcal{L}_i} [\mathcal{L}'_i, L_i]^{1/2} \begin{Bmatrix} \mathcal{L}_{i-1} & L'_i & \mathcal{L}'_i \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix} \times \text{spins.} \tag{C.11}$$

The factor D_6 arises if the relevant subshells of the transition are not adjacent in the series as the angular momenta are coupled, and it accounts for "jumping" over the intervening subshells. The re-ordering the the subshells involves using a product of Wigner 6-j symbols for each intervening subshell for both orbital angular momentum and spin, as shown below:

$$D_6 = \prod_{m=i+1}^{j-1} \delta_{\alpha_m L_m S_m, \alpha'_m L'_m S'_m} (-1)^{l_i+L_m+\mathcal{L}_{m-1}+\mathcal{L}'_m} \times [\mathcal{L}_{m-1}, \mathcal{L}'_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}'_{m-1} & \mathcal{L}_{m-1} \\ L_m & \mathcal{L}_m & \mathcal{L}'_m \end{Bmatrix} \times \text{spins.} \tag{C.12}$$

The factor D_7 includes the reduced matrix element between the relevant subshells as well as terms to recouple the orbital angular momenta of those subshells

to the total orbital angular momenta and to recouple the spins, so that

$$D_7 = \delta_{\mathcal{S}_j,\mathcal{S}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathrm{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathrm{S}'_j]^{1/2}\begin{Bmatrix} \mathcal{S}'_{j-1} & \mathrm{S}'_j & \mathcal{S}_j \\ \mathrm{S}_j & \mathcal{S}_{j-1} & s \end{Bmatrix} \quad \text{(C.13)}$$

$$\times(-1)^{L_j+l_j+L'_j}[\mathcal{L}_{j-1},L'_j,\mathcal{L}_j,\mathcal{L}'_j]^{1/2}\begin{Bmatrix} \mathcal{L}_{j-1} & \mathcal{L}'_{j-1} & l_i \\ L_j & L'_j & l_j \\ \mathcal{L}_j & \mathcal{L}'_j & t \end{Bmatrix}. \quad \text{(C.14)}$$

APPENDIX D
EVALUATION OF ANGULAR PORTION OF $B^{(1)}$.

In this appendix we will simplify the angular portion of $B^{(1)}$, using symmetry properties to reduce the factors outlined in Appendix C. The example of the first order shift, $B^{(1)}$ is an excellent introduction to these methods. Please refer to Appendix C for a description of all notation as well as eqs. C.1, C.2, and C.2. From Section 3.4, we learn that the trace over perturber electron states allows a non-zero result only for the monopole term, $t = 0$, of the multipole expansion. This simplifies the calculation considerably. We return to the examination of $B^{(1)}$ from eq. 3.49 for the case when states α and α' are in the same configuration. Later in this appendix we will refer to eq. 3.52 for cases where they are not in the same configuration. Let us examine eq. 3.49,

$$B^{(1)}_{ii'ff'} = \delta_{ff'} n \lambda_T^3 \int dk\, k^2 e^{-\beta k^2} \sum_l \sum_{s=1}^{q} \delta_{\mathcal{J}\mathcal{J}'} \delta_{\mathcal{M}\mathcal{M}'} \delta_{t0} \frac{[l]^{1/2}}{[\mathcal{J}]^{1/2}} \times$$
$$\mathbf{T}^{\dagger}_{i,\alpha}(\mathcal{J}) D(s) \langle n_s l_s || w_s A'^0(s) C^{(0)}(s) || n_s l_s \rangle \langle k, l || A'^0_1 C^{(0)}_1 || k, l \rangle \mathbf{T}_{\alpha',i'}(\mathcal{J}). \quad \text{(D.1)}$$

In the case where the two states of the matrix elements are in the same configuration, we must first uncouple the total spins, $\mathcal{S}$ and $\mathcal{S}'$, and total orbital angular momenta, $\mathcal{L}$ and $\mathcal{L}'$, from the total angular momentum, $\mathcal{J}$. This can be accomplished using eq. C.2, which is just D_3. We can employ eq. A.19 when an argument of a 6-j symbol is zero. We must remember that a 6-j symbol is unchanged when any two columns are interchanged, as well as if any two numbers in the bottom

row are interchanged with the corresponding two numbers in the top row, so that

$$
\begin{aligned}
D_3 &= \delta_{\mathcal{S}_q,\mathcal{S}'_q}(-1)^{\mathcal{L}_q+\mathcal{S}_q+\mathcal{J'}_q+t}[\mathcal{J'}_q,\mathcal{J}_q]^{1/2}\left\{\begin{array}{ccc}\mathcal{L}_q & \mathcal{S}_q & \mathcal{J}_q\\ \mathcal{J}'_q & 0 & \mathcal{L}'_q\end{array}\right\}\\
&= \delta_{\mathcal{S}_q,\mathcal{S}'_q}(-1)^{\mathcal{L}_q+\mathcal{S}_q+\mathcal{J'}_q+t}[\mathcal{J'}_q,\mathcal{J}_q]^{1/2}\left\{\begin{array}{ccc}\mathcal{L}_q & \mathcal{J}_q & \mathcal{S}_q\\ \mathcal{J}'_q & \mathcal{L}'_q & 0\end{array}\right\}\\
&= \delta_{\mathcal{S}_q,\mathcal{S}'_q}(-1)^{\mathcal{L}_q+\mathcal{S}_q+\mathcal{J'}_q}[\mathcal{J'}_q,\mathcal{J}_q]^{1/2}\delta_{\mathcal{L}_q\mathcal{L}'_q}\delta_{\mathcal{J}_q\mathcal{J}'_q}\\
&\quad (-1)^{\mathcal{L}_q+\mathcal{J}_q+\mathcal{S}_q}[\mathcal{L}_q,\mathcal{J}_q]^{-1/2}. \qquad \text{(D.2)}
\end{aligned}
$$

We know $\mathcal{J}_q$ as simply $\mathcal{J}$, where q represents the total number of subshells summed over. Also, the three arguments in the top row must satisfy a triangle relation and their sum must equal an integer. Therefore the factor, $(-1)^{2\mathcal{L}_q+2\mathcal{S}_q+2\mathcal{J}_q}$ drops out. We are left with the following:

$$
D_3 = \delta_{\mathcal{S}_q,\mathcal{S}'_q}\delta_{\mathcal{L}_q\mathcal{L}'_q}\delta_{\mathcal{J}_q\mathcal{J}'_q}\frac{[\mathcal{J}_q]^{1/2}}{[\mathcal{L}_q]^{1/2}}. \qquad \text{(D.3)}
$$

We continue to uncouple the orbital angular momenta of subshells until arriving at subshell s. These steps are contained in D_4. We will factor out the first term in the product and simplify using the same methods as in D_3. Then, we will continue for the entire product series, as shown below:

$$
\begin{aligned}
D_4 &= \delta_{\alpha_q L_q S_q,\alpha'_q L'_q S'_q}\delta_{S_q,S'_q}(-1)^{\mathcal{L}_{q-1}+L_q+\mathcal{L}'_q+t} \\
&\quad\times[\mathcal{L}_q,\mathcal{L}'_q]^{1/2}\left\{\begin{array}{ccc}\mathcal{L}_{q-1} & L_q & \mathcal{L}_q \\ \mathcal{L}'_q & 0 & \mathcal{L}'_{q-1}\end{array}\right\} \\
&\quad\times\prod_{m=s+1}^{q-1}\delta_{\alpha_m L_m S_m,\alpha'_m L'_m S'_m}\delta_{S_m,S'_m}(-1)^{\mathcal{L}_{m-1}+L_m+\mathcal{L}'_m+t} \\
&\quad\times[\mathcal{L}_m,\mathcal{L}'_m]^{1/2}\left\{\begin{array}{ccc}\mathcal{L}_{m-1} & L_m & \mathcal{L}_m \\ \mathcal{L}'_m & 0 & \mathcal{L}'_{m-1}\end{array}\right\} \\
&= \delta_{\alpha_q L_q S_q,\alpha'_q L'_q S'_q}\delta_{S_q,S'_q}(-1)^{\mathcal{L}_{q-1}+L_q+\mathcal{L}_q}[\mathcal{L}_q,\mathcal{L}_q]^{1/2} \\
&\quad\times\delta_{\mathcal{L}_{q-1}\mathcal{L}'_{q-1}}(-1)^{\mathcal{L}_{q-1}+L_q+\mathcal{L}_q}[\mathcal{L}_{q-1},\mathcal{L}_q]^{-1/2}\prod_{m=s+1}^{q-1}(\cdots\cdots) \\
&= \delta_{\alpha_q L_q S_q,\alpha'_q L'_q S'_q}\delta_{S_q,S'_q}\delta_{\mathcal{L}_{q-1},\mathcal{L}'_{q-1}}\frac{[\mathcal{L}_q]^{1/2}}{[\mathcal{L}_{q-1}]^{1/2}}\prod_{m=s+1}^{q-1}(\cdots) \\
&= \frac{[\mathcal{L}_q]^{1/2}}{[\mathcal{L}_s]^{1/2}}\delta_{\mathcal{L}_s,\mathcal{L}'_s}\prod_{m=s+1}^{q}\delta_{\alpha_m L_m S_m,\alpha'_m L'_m S'_m}\delta_{S_m,S'_m}\delta_{\mathcal{L}_m,\mathcal{L}'_m}. \qquad \text{(D.4)}
\end{aligned}
$$

Thus far, the factors resulting from uncoupling the angular momenta have reduced to a simple expression. We have uncoupled the reduced matrix element up to subshell s, which means we have the following expression:

$$
\begin{aligned}
&\langle\Psi_{\alpha,\mathcal{J}}||w_s A'^0(s)C^{(0)}(s)||\Psi_{\alpha',\mathcal{J}}\rangle \\
&\quad= \frac{[\mathcal{J}]^{1/2}}{[\mathcal{L}_s]^{1/2}}\delta_{\mathcal{L}_s,\mathcal{L}'_s}\prod_{m=s+1}^{q}\delta_{\alpha_m L_m S_m,\alpha'_m L'_m S'_m}\delta_{S_m,S'_m}\delta_{\mathcal{L}_m,\mathcal{L}'_m} \\
&\qquad\times\langle\alpha_{s-1}\mathcal{L}_{s-1}\alpha_s L_s\mathcal{L}_s||A'^0(s)C^{(0)}(s)||\alpha'_{s-1}\mathcal{L}'_{s-1}\alpha'_s L'_s\mathcal{L}'_s\rangle, \qquad \text{(D.5)}
\end{aligned}
$$

which can be uncoupled further by successively applying eq. C.3,

$$\begin{aligned}
&\langle \alpha_{s-1}\mathcal{L}_{s-1}\alpha_s L_s\mathcal{L}_s||A'^0(s)C^{(0)}(s)||\alpha'_{s-1}\mathcal{L}'_{s-1}\alpha'_s L'_s\mathcal{L}'_s\rangle \\
&\quad = \delta_{S_s,S'_s}\delta_{\alpha_{s-1}\mathcal{L}_{s-1},\alpha'_{s-1}\mathcal{L}'_{s-1}}(-1)^{\mathcal{L}_{s-1}+L'_s+\mathcal{L}_s+t}[\mathcal{L}_s,\mathcal{L}'_s]^{1/2}\left\{\begin{array}{ccc} L_s & \mathcal{L}_{s-1} & \mathcal{L}_s \\ t & \mathcal{L}'_s & L'_s \end{array}\right\}\times \\
&\delta_{S_s,S'_s}\sum_L(-1)^{l_s+L+L_s+t}[L_s,L'_s]^{1/2}\left\{\begin{array}{ccc} l_s & L & L_s \\ t & L'_s & l_s \end{array}\right\}\langle n_s l_s||A'^0(s)C^{(0)}(s)||n_s l_s\rangle. \quad \text{(D.6)}
\end{aligned}$$

Setting $t = 0$, we find that these expressions reduce very much like D_4. The 6-j symbols and their accompanying factors drop out leaving $L_s = L'_s$ and a factor of $[\mathcal{L}_s]^{1/2}/[l_s]^{1/2}$,

$$\begin{aligned}
&\langle \alpha_{s-1}\mathcal{L}_{s-1}\alpha_s L_s\mathcal{L}_s||A'^0(s)C^{(0)}(s)||\alpha'_{s-1}\mathcal{L}'_{s-1}\alpha'_s L'_s\mathcal{L}'_s\rangle \\
&\quad = \delta_{S_s,S'_s}\delta_{\mathcal{L}_s,\mathcal{L}'_s}\delta_{S_s,S'_s}\delta_{L_s,L'_s}\frac{[\mathcal{L}_s]^{1/2}}{[l_s]^{1/2}}\langle n_s l_s||A'^0(s)C^{(0)}(s)||n_s l_s\rangle. \quad \text{(D.7)}
\end{aligned}$$

By combining this factor with factors from D_3 and D_4, we get the following result:

$$\begin{aligned}
&\langle \Psi_{\alpha,\mathcal{J}}||A'^0(s)C^{(0)}(s)||\Psi_{\alpha',\mathcal{J}'}\rangle \\
&\quad = \frac{[\mathcal{J}_q]^{1/2}}{[\mathcal{L}_s]^{1/2}}\frac{[\mathcal{L}_s]^{1/2}}{[l_s]^{1/2}}\langle n_s l_s||A'^0(s)C^{(0)}(s)||n_s l_s\rangle\delta_{\mathcal{J}_q\mathcal{J}'_q}\prod_{m=1}^{q}\delta_{\alpha_m L_m \mathrm{S}_m,\alpha'_m L'_m \mathrm{S}'_m}\cdots \\
&\quad = \frac{[\mathcal{J}_q]^{1/2}}{[l_s]^{1/2}}\langle n_s l_s||A'^0(s)C^{(0)}(s)||n_s l_s\rangle\delta_{\mathcal{J}_q\mathcal{J}'_q}\prod_{m=1}^{q}\delta_{\alpha_m L_m \mathrm{S}_m,\alpha'_m L'_m \mathrm{S}'_m}\cdots \quad \text{(D.8)} \\
&D(s) \;=\; \frac{[\mathcal{J}_q]^{1/2}}{[l_s]^{1/2}}\delta_{\alpha\alpha'}. \quad \text{(D.9)}
\end{aligned}$$

Besides reducing to a simple factor, we have shown α and α' must be the same state as well as the same configuration. One can now return this value to

Section 3.4. We will now consider the off-diagonal elements of $B^{(1)}$. D_1 cannot be simplified and will remain as it is in eq C.6. If we make the assumption that there are no more than two electrons within a subshell, D_2 reduces to one. As with the diagonal cases the product of $D_3 \cdot D_4$ reduces to the values obtained in eqs. D.3 and D.4. However, D_5 and D_6 do not offer any simplifications. We must consider some special cases. We will consider three cases with the following notation

$$\begin{aligned}
\cdots l_i^n l_j^0 \cdots &\rightarrow \cdots l_i^{n-1} l_j^1 \cdots \\
\cdots l_i^1 l_j^1 \cdots &\rightarrow \cdots l_i^0 l_j^2 \cdots \\
\cdots l_i^1 l_m^1 l_j^0 \cdots &\rightarrow \cdots l_i^0 l_m^1 l_j^1 \cdots,
\end{aligned}$$

where n is no more than two.

D.1 Case 1:

Examining D_5 for the first case, we become aware that L_i', the total angular momentum of the ith subshell for state α' may only be l_i or zero, depending whether the occupancy is one or zero. It must be remembered that this is also true for the corresponding spin values. As a result, D_5 can have one of the following values: $\mathbf{S_i' = L_i' = 0}$,

$$\begin{aligned}
D_5 \;=\; & \left(\prod_{m=1}^{i-1} \delta_{\alpha_m L_m S_m, \alpha'_m L'_m S'_m} \delta_{\mathcal{L}_m S_m, \mathcal{L}'_m S'_m} \right) (-1)^{\mathcal{L}_{i-1} + L_i' + l_i + \mathcal{L}_i} \\
& [\mathcal{L}_i', L_i]^{1/2} \begin{Bmatrix} \mathcal{L}_{i-1} & 0 & \mathcal{L}_i' \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix} \times \text{spins},
\end{aligned} \tag{D.10}$$

which we may simplify using eq. A.19,

$$
\begin{aligned}
D_5 &= \left(\prod_{m=1}^{i-1}\cdots\right)(-1)^{\mathcal{L}_{i-1}+l_i+\mathcal{L}_i}[\mathcal{L}_i', l_i]^{1/2}\begin{Bmatrix} \mathcal{L}_{i-1} & \mathcal{L}_i & l_i \\ l_i & 0 & \mathcal{L}_i' \end{Bmatrix} \times \text{spins} \\
&= (-1)^{\mathcal{L}_{i-1}+l_i+\mathcal{L}_i}[\mathcal{L}_i', l_i]^{1/2}\delta_{\mathcal{L}_{i-1}\mathcal{L}_i'}(-1)^{\mathcal{L}_{i-1}+\mathcal{L}_i+l_i}[\mathcal{L}_{i-1}, l_i]^{-1/2}\left(\prod_{m=1}^{i-1}\cdots\right) \times \text{spins} \\
&= \left(\prod_{m=1}^{i-1}\cdots\right)\delta_{\mathcal{L}_{i-1}\mathcal{L}_i'}(-1)^{2\mathcal{L}_{i-1}+2l_i+2\mathcal{L}_i} \times \text{spins} \\
&= \left(\prod_{m=1}^{i-1}\cdots\right)\delta_{\mathcal{L}_{i-1}\mathcal{L}_i'}\delta_{\mathcal{S}_{i-1}\mathcal{S}_i'}, \qquad \text{(D.11)}
\end{aligned}
$$

or $\mathbf{L_i'} = \mathbf{l_i}, \mathbf{S_i'} = \mathbf{s}$,

$$
\begin{aligned}
D_5 &= \left(\prod_{m=1}^{i-1}\delta_{\alpha_m L_m S_m, \alpha_m' L_m' S_m'}\delta_{\mathcal{L}_m \mathcal{S}_m, \mathcal{L}_m' \mathcal{S}_m'}\right)(-1)^{\mathcal{L}_{i-1}+2l_i+\mathcal{L}_i} \\
&\quad [\mathcal{L}_i', L_i]^{1/2}\begin{Bmatrix} \mathcal{L}_{i-1} & l_i & \mathcal{L}_i' \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix} \times \text{spins} \qquad \text{(D.12)}
\end{aligned}
$$

Therefore, D_5 simplifies for the case resembling a hydrogenic model, but not for more complex cases. When considering D_6, we notice $L_m = 0$ for any intervening subshells. As a result, D_6 reduces to one. We now turn to D_7, we remember that we have already discovered from Section 3.4 that $l_i = l_j$. we may use eq. A.22 to simplify D_7,

$$
\begin{aligned}
D_7 &= \delta_{\mathcal{S}_j,\mathcal{S}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathcal{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathcal{S}'_j]^{1/2}
\left\{ \begin{array}{ccc} \mathcal{S}'_{j-1} & \mathcal{S}'_j & \mathcal{S}_j \\ \mathcal{S}_j & \mathcal{S}_{j-1} & s \end{array} \right\} \\
&\quad \times(-1)^{L_j+l_j+L'_j}[\mathcal{L}_{j-1},L'_j,\mathcal{L}_j,\mathcal{L}'_j]^{1/2}
\left\{ \begin{array}{ccc} \mathcal{L}_{j-1} & \mathcal{L}'_{j-1} & l_i \\ L_j & L'_j & l_i \\ \mathcal{L}_j & \mathcal{L}'_j & 0 \end{array} \right\} \\
&= \delta_{\mathcal{S}_j,\mathcal{S}'_j}\delta_{\mathcal{L}_j\mathcal{L}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathcal{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathcal{S}'_j]^{1/2}
\left\{ \begin{array}{ccc} \mathcal{S}'_{j-1} & \mathcal{S}'_j & \mathcal{S}_j \\ \mathrm{S}_j & \mathcal{S}_{j-1} & s \end{array} \right\} \\
&\quad \times(-1)^{2L_j+2l_i+L'_j+\mathcal{L}'_{j-1}+\mathcal{L}_j}\frac{[\mathcal{L}_{j-1},L'_j,\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}
\left\{ \begin{array}{ccc} \mathcal{L}_{j-1} & \mathcal{L}'_{j-1} & l_i \\ L'_j & L_j & \mathcal{L}_j \end{array} \right\}. \qquad \text{(D.13)}
\end{aligned}
$$

We know $\mathcal{L}_j$ must equal $\mathcal{L}'_j$ so that the triangle relations of that row are satisfied. Although this is an improvement, we must examine the other terms to determine if we can simplify the expression further. D_7 may be simplified because $L_j = \mathrm{S_j} = 0$, and $L'_j = l_j = l_i$, with corresponding values for spin. We also remember that $j-1 = i$

$$
\begin{aligned}
D_7 &= \delta_{\mathcal{S}_j,\mathcal{S}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathcal{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathrm{S}'_j]^{1/2}
\left\{ \begin{array}{ccc} \mathcal{S}'_{j-1} & \mathrm{S}'_j & \mathcal{S}_j \\ 0 & \mathcal{S}_{j-1} & s \end{array} \right\} \\
&\quad \times(-1)^{2l_i+L'_j+\mathcal{L}'_{j-1}+\mathcal{L}_j}\frac{[\mathcal{L}_{j-1},l_i,\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}
\left\{ \begin{array}{ccc} \mathcal{L}_{j-1} & \mathcal{L}'_{j-1} & l_i \\ L'_j & 0 & \mathcal{L}_j \end{array} \right\} \\
&= \delta_{\mathcal{S}_j,\mathcal{S}'_j}\delta_{l_i,l_j}\delta_{\mathcal{L}_j\mathcal{L}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathcal{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathrm{S}'_j]^{1/2}\delta_{\mathrm{S}'_j s}\delta_{\mathcal{S}_j\mathcal{S}_{j-1}}(-1)^{\mathcal{S}'_{j-1}+\mathcal{S}'_j+\mathcal{S}_j}[\mathrm{S}'_j,\mathcal{S}_j]^{-1/2} \\
&\quad (-1)^{3l_i+\mathcal{L}'_{j-1}+\mathcal{L}_j}[\mathcal{L}_i,\mathcal{L}_j]^{1/2}\delta_{\mathcal{L}_{j-1}\mathcal{L}_j}(-1)^{\mathcal{L}_{j-1}+\mathcal{L}'_{j-1}+l_i}[\mathcal{L}_{j-1}l_i]^{-1/2}, \qquad \text{(D.14)}
\end{aligned}
$$

which can be reduced further,

$$\begin{aligned} D_7 &= \delta_{S_j,S'_j}\delta_{S'_j s}\delta_{S_j S_{j-1}}(-1)^{2S'_i+2S'_j+2S_j}\delta_{l_i,l_j}\delta_{\mathcal{L}_j\mathcal{L}'_j}\delta_{\mathcal{L}_i\mathcal{L}_j}(-1)^{2\mathcal{L}'_i+2\mathcal{L}_i}\frac{[\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}} \\ &= \delta_{S_j,S'_j}\delta_{S'_j s}\delta_{S_j S_{j-1}}\delta_{l_i,l_j}\delta_{\mathcal{L}_j\mathcal{L}'_j}\delta_{\mathcal{L}_i\mathcal{L}_j}\frac{[\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}. \end{aligned} \tag{D.15}$$

We may now multiply the factors together to get the following expression, $S'_i = L'_i = 0$,

$$\begin{aligned} D_1\cdots D_7 &= \frac{[\mathcal{J}_q]^{1/2}}{[\mathcal{L}_q]^{1/2}}\frac{[\mathcal{L}_q]^{1/2}}{[\mathcal{L}_j]^{1/2}}\frac{[\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}\delta_{S_j S_i}\delta_{l_i,l_j}\delta_{\mathcal{L}_i\mathcal{L}_j}\delta_{\mathcal{J}\mathcal{J}'}\delta_{S_j,S'_j}\delta_{\mathcal{L}_j,\mathcal{L}'_j} \\ &\quad \prod_{m=j+1}^{q}\delta_{\alpha_m L_m S_m,\alpha'_m L'_m S'_m}\delta_{S_m,S'_m}\delta_{\mathcal{L}_m,\mathcal{L}'_m} \\ &\quad \left(\prod_{n=1}^{i-1}\delta_{\alpha_n L_n S_n,\alpha'_n L'_n S'_n}\delta_{\mathcal{L}_n S_n,\mathcal{L}'_n S'_n}\right) \\ &= \frac{[\mathcal{J}_q]^{1/2}}{[l_i]^{1/2}}\delta_{S_j S_i}\cdots, \end{aligned} \tag{D.16}$$

$\mathbf{L}'_i = \mathbf{l}_i, \mathbf{S}'_i = \mathbf{s}$,

$$\begin{aligned} D_1\cdots D_7 &= (n\cdot k)^{1/2}(-1)^{\Delta p}\frac{[\mathcal{J}_q]^{1/2}}{[l_i]^{1/2}}(-1)^{\mathcal{L}_{i-1}+\mathcal{L}_i}[\mathcal{L}'_i, L_i]^{1/2}\begin{Bmatrix} \mathcal{L}_{i-1} & l_i & \mathcal{L}'_i \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix} \\ &\quad \times\text{spins}\times\delta_{S_j S_i}\cdots. \end{aligned} \tag{D.17}$$

D.2 Case 2:

With respect to case 2, we may use our results for D_5 when $L'_i = 0$ in eq. D.11, which is very simple, and the same results for D_6, that the factor equals one. We

now remember $L_j = l_j = l_i$ and $\mathrm{S}_j = s$ and consider D_7,

$$D_7 = \delta_{\mathcal{S}_j,\mathcal{S}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathrm{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathrm{S}'_j]^{1/2}\begin{Bmatrix} \mathcal{S}'_{j-1} & \mathrm{S}'_j & \mathcal{S}_j \\ \mathrm{S}_j & \mathcal{S}_{j-1} & s \end{Bmatrix} \tag{D.18}$$

$$\times(-1)^{2L_j+2l_i+L'_j+\mathcal{L}'_{j-1}+\mathcal{L}_j}\frac{[\mathcal{L}_{j-1},L'_j,\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}\begin{Bmatrix} \mathcal{L}_{j-1} & \mathcal{L}'_{j-1} & l_i \\ L'_j & L_j & \mathcal{L}_j \end{Bmatrix}$$

$$= \delta_{\mathcal{S}_j,\mathcal{S}'_j}(-1)^{\mathcal{S}'_{j-1}+\mathrm{S}'_j+\mathcal{S}_j}[\mathcal{S}_{j-1},\mathrm{S}'_j]^{1/2}\begin{Bmatrix} \mathcal{S}'_{j-1} & s & \mathcal{S}_{j-1} \\ s & \mathcal{S}_j & \mathrm{S}'_j \end{Bmatrix} \tag{D.19}$$

$$\times(-1)^{\mathcal{L}'_{j-1}+L'_j+\mathcal{L}_j}\frac{[\mathcal{L}_{j-1},L'_j,\mathcal{L}_j]^{1/2}}{[l_i]^{1/2}}\begin{Bmatrix} \mathcal{L}'_{j-1} & l_i & \mathcal{L}_{j-1} \\ l_i & \mathcal{L}_j & L'_j \end{Bmatrix}. \tag{D.20}$$

We have arranged the argument order so that the two 6-j symbols resemble each other and the result for D_5 from Case 1. In fact, result for the entire product will be very similar,

$$D_1\cdots D_7 = (n\cdot k)(-1)^{\Delta_P}\frac{[\mathcal{J}_0]^{1/2}}{[l_i]^{1/2}}(-1)^{\mathcal{L}'_{j-1}+L'_j+\mathcal{L}_j}[\mathcal{L}_{j-1},L'_j]^{1/2}$$

$$\times\begin{Bmatrix} \mathcal{L}'_{j-1} & l_i & \mathcal{L}_{j-1} \\ l_i & \mathcal{L}_j & L'_j \end{Bmatrix}\times\text{spins}\times\delta_{\mathcal{L}_j\mathcal{L}'_j}\cdots. \tag{D.21}$$

D.3 Case 3:

In the third and final case, we find D_5 and D_7 have their simplest solutions from eqs. D.11 and D.15, although we cannot say $j-1=i$, rather $j-1=m$. However, we must consider D_6, using the fact that $L_m = l_m$, $\mathcal{L}_{m-1} = \mathcal{L}_i$, and

$\mathcal{L}'_{m-1} = \mathcal{L}'_i$ and the corresponding values for spin,

$$D_6 = \delta_{\alpha_m L_m S_m, \alpha'_m L'_m S'_m} (-1)^{l_i + l_m + \mathcal{L}_i + \mathcal{L}'_m} \times [\mathcal{L}_i, \mathcal{L}'_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}'_i & \mathcal{L}_i \\ l_m & \mathcal{L}_m & \mathcal{L}'_m \end{Bmatrix} \times \text{spins}. \tag{D.22}$$

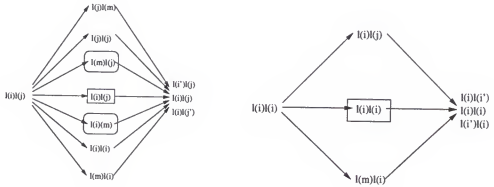
Combining our results, we obtain the following expression:

$$D_1 \cdots D_7 = (n \cdot k)(-1)^{\Delta p} \frac{[\mathcal{J}_q]^{1/2}}{[l_i]^{1/2}} (-1)^{\mathcal{L}_i + l_i + l_m + \mathcal{L}'_m} [\mathcal{L}_i, \mathcal{L}'_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}'_i & \mathcal{L}_i \\ l_m & \mathcal{L}_m & \mathcal{L}'_m \end{Bmatrix} \times \text{spins} \times \delta_{\mathcal{L}_j \mathcal{L}_m} \cdots. \tag{D.23}$$

As one can see, the transitions with doubly occupied manifolds are more complicated that those with no more than singly occupied subshells, but these three cases can be reduced to forms much simpler than the original. Note that all the subshells other than j and i have the same quantum numbers (α_m, L_m, and S_m) for states α and α'. This confirms our conjecture that since $l_i = l_j$ the off-diagon terms must be non-zero only between states within a Rydberg series. Many of the solutions we have obtained for D_5 and D_6 will be applied to the second order terms as well.

APPENDIX E
EVALUATION OF ANGULAR PORTION OF $D_{l,l'',l'}(K_1, K_2)$

In this appendix, we will evaluate the angular matrix elements of the operator second order in the radiator-perturbing electron potential, $D_{i,i'',i'}(k_1, k_2)$. Please refer to Appendix C for a description of all notation. In Figure E, a schematic has been drawn to show the cases one must sum over to calculate the second order term for the case where no more than two electrons are allowed to interact. There may be other electrons in other manifolds, but we will only consider those cases where the contributions from other manifolds are minimal. The α'' states contained in the rectangular boxes are of the same configuration as the states α and α' while not necessarily identical. The terms contained in rounded boxes are "near-hydrogenic," in the sense that an electron is undergoing a transition from a singly occupied subshell to an empty subshell without crossing any occupied subshells.



In the case where the two states of the matrix elements are in the same configuration, we may refer to Appendix D for guidance. We have the same factors; although we cannot set the multipole index t to zero. However, we may take advantage of sum rules to simplify our expression.

E.1 Single Configuration, Non-Transitioning Matrix Elements

In this section, we will simplify the expression for $D_{i,i'',i'}(k_1,k_2)$ in eq. 3.69 first by reexpressing the sum over individual electrons to a sum over subshells using eq. 3.39. We define the quantity, $\mathbf{A}'^{(t)} \cdot \mathbf{A}'^{(t)}_{\alpha,\alpha'}$ as follows,

$$\begin{aligned}\mathbf{A}'^{(t)} \cdot \mathbf{A}'^{(t)}_{\alpha,\alpha'} &= \sum_{\alpha''} \sum_{s=1}^{q} \sum_{r=1}^{q} \langle \Psi_{\alpha,\mathcal{J}} || w_s A'^{(t)}(s) C^{(t)}(s) || \Psi_{\alpha'',\mathcal{J}''} \rangle \\ &\quad \langle \Psi_{\alpha',\mathcal{J}} || w_r A'^{(t)}(r) C^{(t)}(r) || \Psi_{\alpha'',\mathcal{J}''} \rangle^*. \end{aligned} \tag{E.1}$$

This expression can be reduced to a collection of sums dependent on whether s is higher, lower, or equal to r, as shown the the expression below.

$$\begin{aligned}\mathbf{A}'^{(t)} \cdot \mathbf{A}'^{(t)}_{\alpha,\alpha'} &= \sum_{r=1}^{q} \sum_{s<r} D(s,r) w_s w_r A'^{(t)}_{n_s l_s n_s l_s} A'^{(t)}_{n_r l_r n_r l_r} \\ &\quad + \sum_{r=1}^{q} D(r,r) w_r^2 (A'^{(t)}_{n_r l_r n_r l_r})^2 + \sum_{r=1}^{q} \sum_{s>r} D(r,s) w_s w_r A'^{(t)}_{n_r l_r n_r l_r} A'^{(t)}_{n_s l_s n_s l_s}, \end{aligned} \tag{E.2}$$

where

$$A'^{(t)}_{n_s l_s n_s l_s} = \langle n_s l_s || A'^{t}(s) C^{(t)}(s) || n_s l_s \rangle. \tag{E.3}$$

In order to obtain the factors $D(r,r)$ and $D(s,r)$, we must uncouple the angular momenta as we did in Appendix D. We will continue to make our simplifying assumption that there are no more than two electrons within a subshell. We now uncouple the total spins and total orbital angular momenta from the total angular momentum, $\mathcal{J}$ by reducing the product $D_3 \cdot D_3$, where D_3 is defined in eq. C.9,

$$\begin{aligned} D_3 \cdot D_3 &= \delta_{\mathcal{S}_q,\mathcal{S}_q''}(-1)^{\mathcal{L}_q+\mathcal{S}_q+\mathcal{J}_q''+t}[\mathcal{J}_q,\mathcal{J}_q'']^{1/2}\begin{Bmatrix} \mathcal{L}_q & \mathcal{S}_q & \mathcal{J}_q \\ \mathcal{J}_q'' & t & \mathcal{L}_q'' \end{Bmatrix} \\ &\times\delta_{\mathcal{S}_q'',\mathcal{S}_q'}(-1)^{-\mathcal{L}_q'-\mathcal{S}_q'-\mathcal{J}_q''-t}[\mathcal{J}_q',\mathcal{J}_q'']^{1/2}\begin{Bmatrix} \mathcal{L}_q' & \mathcal{S}_q' & \mathcal{J}_q' \\ \mathcal{J}_q'' & t & \mathcal{L}_q'' \end{Bmatrix}. \end{aligned} \tag{E.4}$$

We know $\mathcal{J}_q$ as simply $\mathcal{J}$, where q represents the total number of subshells summed over. We will employ the completeness relation written in eq. A.17 that takes advantage of the fact that $\mathcal{S}_q = \mathcal{S}_q'' = \mathcal{S}_q'$ and $\mathcal{J} = \mathcal{J}'$. We also use the symmetry relations that a 6-j symbol is unchanged if any two columns are interchanged, as well as if any two numbers in the bottom row are interchanged with the corresponding two numbers in the top row,

$$\begin{aligned} D_3 \cdot D_3 &= \delta_{\mathcal{S}_q,\mathcal{S}_q''}\delta_{\mathcal{S}_q'',\mathcal{S}_q'}(-1)^{\mathcal{L}_q-\mathcal{L}_q'}[\mathcal{J}_q,\mathcal{J}_q''] \\ &\qquad \begin{Bmatrix} \mathcal{L}_q'' & \mathcal{S}_q & \mathcal{J}_q'' \\ \mathcal{J}_q & t & \mathcal{L}_q \end{Bmatrix}\begin{Bmatrix} \mathcal{L}_q'' & \mathcal{S}_q & \mathcal{J}_q'' \\ \mathcal{J}_q & t & \mathcal{L}_q' \end{Bmatrix} \\ \sum_{\mathcal{J}_q''} D_3 \cdot D_3 &= \delta_{\mathcal{S}_q,\mathcal{S}_q''}\delta_{\mathcal{S}_q'',\mathcal{S}_q'}\delta_{\mathcal{L}_q,\mathcal{L}_q'}\frac{[\mathcal{J}_q]}{[\mathcal{L}_q]}. \end{aligned} \tag{E.5}$$

This simplifies well, and we will find that $D_4 \cdot D_4$ simplifies well also, until we must treat the relevant subshell. We write $D_4 \cdot D_4$ as follows:

$$
\begin{aligned}
D_4 \cdot D_4 \;=\; & \prod_{m=s+1}^{q} \prod_{n=r+1}^{q} \delta_{\alpha_m L_m \mathrm{S}_m, \alpha''_m L''_m S''_m} \delta_{\mathcal{S}_m, \mathcal{S}''_m} \delta_{\alpha''_n L''_n S''_n, \alpha'_n L'_n S'_n} \delta_{\mathcal{S}''_n, \mathcal{S}'_n} \\
& (-1)^{\mathcal{L}_{m-1}+L_m+\mathcal{L}''_m+t} (-1)^{-\mathcal{L}'_{n-1}-L'_n-\mathcal{L}''_n-t} [\mathcal{L}_m, \mathcal{L}''_m]^{1/2} [\mathcal{L}''_n, \mathcal{L}'_n]^{1/2} \\
& \left\{ \begin{array}{ccc} \mathcal{L}_{m-1} & L_m & \mathcal{L}_m \\ \mathcal{L}''_m & t & \mathcal{L}''_{m-1} \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}'_{n-1} & L'_n & \mathcal{L}'_n \\ \mathcal{L}''_n & t & \mathcal{L}''_{n-1} \end{array} \right\}. \qquad \text{(E.6)}
\end{aligned}
$$

Taking advantage of the Kronecker deltas from $D_3 \cdot D_3$, we factor out the terms related to the qth subshell and take the sum over $\mathcal{L}''_q$,

$$
\begin{aligned}
D_4 \cdot D_4 = {} & \delta_{\alpha_q L_q \mathrm{S}_q, \alpha''_q L''_q S''_q} \delta_{\mathcal{S}_q, \mathcal{S}''_q} (-1)^{\mathcal{L}_{q-1}+L_q+\mathcal{L}''_q+t} [\mathcal{L}_q, \mathcal{L}''_q]^{1/2} \\
& \delta_{\alpha''_q L''_q S''_q, \alpha'_q L'_q S'_q} \delta_{\mathcal{S}''_q, \mathcal{S}'_q} (-1)^{-\mathcal{L}'_{q-1}-L'_q-\mathcal{L}''_q-t} [\mathcal{L}''_q, \mathcal{L}'_q]^{1/2} \\
& \left\{ \begin{array}{ccc} \mathcal{L}''_{q-1} & L_q & \mathcal{L}''_q \\ \mathcal{L}_q & t & \mathcal{L}_{q-1} \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}''_{q-1} & L_q & \mathcal{L}''_q \\ \mathcal{L}'_q & t & \mathcal{L}'_{q-1} \end{array} \right\} \\
& \left(\prod_{m=s+1}^{q-1} \cdots \right) \left(\prod_{m=r+1}^{q-1} \cdots \right). \qquad \text{(E.7)}
\end{aligned}
$$

We can take advantage of the relations $L_q = L''_q = L'_q$ and $\mathcal{L}'_q = \mathcal{L}_q$ to help us simplify, using eq. A.17,

$$
\begin{aligned}
\sum_{\mathcal{L}''_q} D_4 \cdot D_4 \;=\; & \delta_{\alpha_q L_q \mathrm{S}_q, \alpha'_q L''_q S''_q} \delta_{\alpha''_q L''_q S''_q, \alpha'_q L'_q S'_q} \delta_{\mathcal{L}_q, \mathcal{L}'_q} \\
& \delta_{\mathcal{L}_{q-1}, \mathcal{L}'_{q-1}} \frac{[\mathcal{L}_q]}{[\mathcal{L}_{q-1}]} \left(\prod_{m=s+1}^{q-1} \cdots \right) \left(\prod_{m=r+1}^{q-1} \cdots \right). \qquad \text{(E.8)}
\end{aligned}
$$

We can successively reduce each set of 6-j symbols until we reach either subshell s or r. For the moment we will assume r is the higher subshell. First, let us write the reduced $D_4 \cdot D_4$ up to subshell r,

$$\sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{r+1}} D_4 \cdot D_4 = \delta_{\mathcal{L}_r,\mathcal{L}'_r} \frac{[\mathcal{L}_q]}{[\mathcal{L}_r]} \prod_{m=s+1}^{r} \delta_{\alpha_m L_m \mathrm{S}_m,\alpha''_m L''_m \mathrm{S}''_m} \delta_{\mathcal{S}_m,\mathcal{S}''_m}$$
$$(-1)^{\mathcal{L}_{m-1}+L_m+\mathcal{L}''_m+t}[\mathcal{L}_m,\mathcal{L}''_m]^{1/2} \begin{Bmatrix} \mathcal{L}_{m-1} & L_m & \mathcal{L}_m \\ \mathcal{L}''_m & t & \mathcal{L}''_{m-1} \end{Bmatrix}$$
$$\prod_{n=r+1}^{q} \delta_{\alpha_n L_n \mathrm{S}_n,\alpha''_n L''_n \mathrm{S}''_n} \delta_{\alpha''_n L''_n \mathrm{S}''_n,\alpha'_n L'_n \mathrm{S}'_n} \delta_{\mathcal{L}_n,\mathcal{L}'_n} \delta_{\mathcal{S}_n,\mathcal{S}''_n} \delta_{\mathcal{S}''_n,\mathcal{S}'_n}. \quad \text{(E.9)}$$

If $r = s$, the product series drops out and we may examine the remaining matrix elements. If $r \neq s$, we must retain this product series as a factor of $D(s,r)$. We can find some symmetries, although the expression seems difficult to simplify. For example, we will show $D(s,r) = D(r,s)$. Before we can show this, let us examine the factor that arises from uncoupling the angular momenta of the last electrons in subshells r and s respectively,

$$D(s,r) = D_3 \cdot D_3 D_4 \cdot D_4 \delta_{\mathcal{S}_s,\mathcal{S}''_s} \delta_{\mathcal{S}''_s,\mathcal{S}'_r} \delta_{\alpha_{s-1}\mathcal{L}_{s-1},\alpha''_{s-1}\mathcal{L}''_{s-1}} \delta_{\alpha''_{r-1}\mathcal{L}''_{r-1},\alpha'_{r-1}\mathcal{L}'_{r-1}}$$
$$\delta_{\mathrm{S}_s,\mathrm{S}''_s} \delta_{\mathrm{S}''_r,\mathrm{S}'_r} \sum_{L} \sum_{L'} (-1)^{\mathcal{L}_{s-1}+L''_s+\mathcal{L}_s+t} (-1)^{-\mathcal{L}'_{r-1}-L''_r-\mathcal{L}'_r-t}$$
$$(-1)^{l_s+L+L_s+t} (-1)^{-l_r-L'-L'_r-t} [\mathcal{L}_s,\mathcal{L}''_s]^{1/2} [\mathcal{L}''_r,\mathcal{L}'_r]^{1/2} [L_s,L''_s]^{1/2} [L''_r,L'_r]^{1/2}$$
$$\begin{Bmatrix} \mathcal{L}_{s-1} & L_s & \mathcal{L}_s \\ t & \mathcal{L}''_s & L''_s \end{Bmatrix} \begin{Bmatrix} \mathcal{L}'_{r-1} & L'_r & \mathcal{L}'_r \\ t & \mathcal{L}''_r & L''_r \end{Bmatrix} \begin{Bmatrix} L & l_s & L_s \\ t & L''_s & l_s \end{Bmatrix} \begin{Bmatrix} L' & l_r & L'_r \\ t & L''_r & l_r \end{Bmatrix} \quad \text{(E.10)}$$

where the sums over L and L' represent the the intermediate sums over angular momenta before that of the last electrons within subshells s and r respectively are

included. In this work, we have chosen to consider cases where there are no more than two electrons in a given subshell, therefore, $L = L' = 0$ if the subshell is singly occupied or $L = l_s$ and $L' = l_r$ if doubly occupied, so the sum reduces to a single term.

We can consider two cases, $r = s$ and $r \neq s$. If $r = s$, we may sum over $L''_s = L''_r$ and $\mathcal{L}''_s = \mathcal{L}''_r$ Also, from eq. E.9, we know $\mathcal{L}_r = \mathcal{L}'_r$ and $\mathcal{L}_{r-1} = \mathcal{L}'_{r-1}$ since all subshells below r are in the same state. We express $D(r,r)$ as follows:

$$
\begin{aligned}
D(r,r) &= D_3 \cdot D_3 D_4 \cdot D_4 \sum_{\mathcal{L}''_r} \sum_{L''_r} (-1)^{L_r - L'_r} [\mathcal{L}_r, \mathcal{L}''_r][L_r, L''_r]^{1/2} [L''_r, L'_r]^{1/2} \times \\
&\quad \left\{ \begin{array}{ccc} \mathcal{L}_{r-1} & L_r & \mathcal{L}_r \\ t & \mathcal{L}''_r & L''_r \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}'_{r-1} & L'_r & \mathcal{L}'_r \\ t & \mathcal{L}''_r & L''_r \end{array} \right\} \left\{ \begin{array}{ccc} L & l_r & L_r \\ t & L''_r & l_r \end{array} \right\} \left\{ \begin{array}{ccc} L & l_r & L'_r \\ t & L''_r & l_r \end{array} \right\} \\
&= \frac{[\mathcal{J}_q]}{[\mathcal{L}_q]} \frac{[\mathcal{L}_q]}{[\mathcal{L}_r]} \sum_{L''_r} \delta_{L'_r, L_r} [\mathcal{L}_r, L''_r] \left\{ \begin{array}{ccc} L & l_r & L''_r \\ t & L_r & l_r \end{array} \right\} \left\{ \begin{array}{ccc} L & l_r & L''_r \\ t & L_r & l_r \end{array} \right\} \\
&= \delta_{L'_r, L_r} \frac{[\mathcal{J}_q]}{[\mathcal{L}_r]} \frac{[\mathcal{L}_r]}{[l_r]} \qquad \text{(E.11)} \\
D(r,r) &= \frac{[\mathcal{J}_q]}{[l_r]} \delta_{\alpha\alpha'}. \qquad \text{(E.12)}
\end{aligned}
$$

We see that $D(r,r)$ reduces to simple terms, we now examine $D(s,r)$ The next step is to show that $D(s,r) = D(r,s)$. We cannot simplify much but we may reduce two 6-j symbols to one symbol using eq. A.18. We first write down the 6-j symbol dependent on $\mathcal{L}'_{r-1}$ in eq. E.10 and its accompanying factors and factor from $D_4 \cdot D_4$ We can conclude from eq. E.10 that α'' is in the same state as α' for all subshells below r , which we can use to simplify the expression, so that

$\mathcal{L}''_{r-1} = \mathcal{L}'_{r-1}$ where $m = r$. Also, from eq. E.9, $L_r = L''_r$.

$$\begin{aligned}
&\sum_{\mathcal{L}''_r} (-1)^{-\mathcal{L}'_{r-1}-L''_r-\mathcal{L}'_r-t}(-1)^{\mathcal{L}_{r-1}+L_r+\mathcal{L}''_r+t}[\mathcal{L}''_r,\mathcal{L}'_r]^{1/2}[\mathcal{L}_r,\mathcal{L}''_r]^{1/2} \\
&\qquad \left\{ \begin{array}{ccc} \mathcal{L}'_{r-1} & L'_r & \mathcal{L}'_r \\ t & \mathcal{L}''_r & L''_r \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_{r-1} & L_r & \mathcal{L}_r \\ \mathcal{L}''_r & t & \mathcal{L}''_{r-1} \end{array} \right\} \\
&= (-1)^{\mathcal{L}_{r-1}-\mathcal{L}'_{r-1}+\mathcal{L}''_r-\mathcal{L}_r}[\mathcal{L}_r,\mathcal{L}''_r] \left\{ \begin{array}{ccc} \mathcal{L}_r & \mathcal{L}'_{r-1} & L'_r \\ L_r & t & \mathcal{L}''_r \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_r & L_r & \mathcal{L}_{r-1} \\ \mathcal{L}'_{r-1} & t & \mathcal{L}''_r \end{array} \right\} \\
&= (-1)^{-L'_r-\mathcal{L}'_{r-1}-\mathcal{L}_r}[\mathcal{L}_r] \left\{ \begin{array}{ccc} \mathcal{L}_r & \mathcal{L}'_{r-1} & L'_r \\ t & L_r & \mathcal{L}_{r-1} \end{array} \right\} \qquad \text{(E.13)}
\end{aligned}$$

As we substitute this expression into eq. E.10 we remember $L''_m = L'_m$ and $\mathcal{L}''_m = \mathcal{L}'_m$ when m is less than r.

$$\begin{aligned}
D(s,r) &= \frac{[\mathcal{J}_q]}{[\mathcal{L}_r]} \delta_{S_s,S''_s}\delta_{S''_r,S_r}\delta_{\alpha_{s-1}\mathcal{L}_{s-1},\alpha''_{s-1}\mathcal{L}''_{s-1}}\delta_{\alpha''_{r-1}\mathcal{L}''_{r-1},\alpha'_{r-1}\mathcal{L}'_{r-1}} \\
&\quad \delta_{S_s,S''_s}\delta_{S''_r,S_r} \sum_L \sum_{L'} (-1)^{\mathcal{L}_{s-1}-\mathcal{L}_r}(-1)^{L_s+L'_s+\mathcal{L}_s-\mathcal{L}'_{r-1}+t} \\
&\quad (-1)^{l_s-l_r+L-L'}[\mathcal{L}_s,\mathcal{L}'_s]^{1/2}[\mathcal{L}_r][L_s,L'_s]^{1/2}[L_r,L'_r]^{1/2} \\
&\quad \left\{ \begin{array}{ccc} \mathcal{L}_{s-1} & L_s & \mathcal{L}_s \\ t & \mathcal{L}'_s & L'_s \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_r & L'_r & \mathcal{L}'_{r-1} \\ t & \mathcal{L}_{r-1} & L_r \end{array} \right\} \\
&\quad \left\{ \begin{array}{ccc} L & l_s & L_s \\ t & L'_s & l_s \end{array} \right\} \left\{ \begin{array}{ccc} L' & l_r & L'_r \\ t & L_r & l_r \end{array} \right\} \\
&\quad \times \prod_{m=s+1}^{r-1} \delta_{\alpha_m L_m S_m,\alpha''_m L''_m S''_m}\delta_{S_m,S''_m}(-1)^{\mathcal{L}_{m-1}+L_m+\mathcal{L}'_m+t} \\
&\quad [\mathcal{L}_m,\mathcal{L}'_m]^{1/2} \left\{ \begin{array}{ccc} \mathcal{L}_{m-1} & L_m & \mathcal{L}_m \\ \mathcal{L}'_m & t & \mathcal{L}'_{m-1} \end{array} \right\}. \qquad \text{(E.14)}
\end{aligned}$$

If we exchange $L_s \to L'_s$, $L_r \to L'_r$, and so forth, we find $D(r,s) = D(s,r)$ as long as any subshell between r and s contains no more than one electron. This is possible because $L_m = L'_m = l_m$ or the subshell orbital angular momentum equals zero.

Let us consider two practical examples, a Li-like satellite of a He-like transition $nln'l'1s \to n'l'1s^2$ and a Be-like transition $nl2l'1s^2 \to 2l'2l''1s^2$. If subshell s is the $1s$ orbital and subshell r is the nl orbital the result simplifies considerably because $L_s = L'_s = \mathcal{L}_{s-1} = \mathcal{L}_s = 0$. We will now reduce the four 6-j symbols and their accompanying factors,

$$
\begin{aligned}
&(-1)^{\mathcal{L}_{s-1}-\mathcal{L}_r}(-1)^{L_s+L'_s+\mathcal{L}_s-\mathcal{L}'_{r-1}+t} \\
&(-1)^{l_s-l_r+L-L'}[\mathcal{L}_s,\mathcal{L}'_s]^{1/2}[\mathcal{L}_r][L_s,L'_s]^{1/2}[L_r,L'_r]^{1/2} \\
&\begin{Bmatrix} \mathcal{L}_{s-1} & L_s & \mathcal{L}_s \\ t & \mathcal{L}'_s & L'_s \end{Bmatrix}
\begin{Bmatrix} \mathcal{L}_r & L'_r & \mathcal{L}'_{r-1} \\ t & \mathcal{L}_{r-1} & L_r \end{Bmatrix} \\
&\begin{Bmatrix} L & l_s & L_s \\ t & L'_s & l_s \end{Bmatrix}
\begin{Bmatrix} L' & l_r & L'_r \\ t & L_r & l_r \end{Bmatrix} \\
&\qquad = \delta_{t0}(-1)^{-\mathcal{L}_r-\mathcal{L}'_{r-1}}(-1)^{-l_r-L'}[\mathcal{L}_r][L_r,L'_r]^{1/2} \\
&\qquad\qquad \begin{Bmatrix} \mathcal{L}_r & L'_r & \mathcal{L}'_{r-1} \\ 0 & \mathcal{L}_{r-1} & L_r \end{Bmatrix}
\begin{Bmatrix} L' & l_r & L'_r \\ 0 & L_r & l_r \end{Bmatrix} \\
&\qquad = \delta_{t0}\delta_{\mathcal{L}_{r-1}\mathcal{L}'_{r-1}}\delta_{L_rL'_r}\frac{[\mathcal{L}_r]}{[\mathcal{L}_{r-1},l_r]^{1/2}}. \qquad \text{(E.15)}
\end{aligned}
$$

If we evaluate the factor arising from $D_4 \cdot D_4$, we get the following solution:

$$
\begin{aligned}
D(1s,nl) &= \delta_{t0}\delta_{\alpha\alpha'}\frac{[\mathcal{J}_q]}{[\mathcal{L}_r]}\frac{[\mathcal{L}_r]}{[\mathcal{L}_{r-1},l_r]^{1/2}}(-1)^{\mathcal{L}_s+L_{r-1}+\mathcal{L}'_{r-1}+t} \\
&\quad [\mathcal{L}_{r-1},\mathcal{L}'_{r-1}]^{1/2}\left\{\begin{array}{ccc} \mathcal{L}_s & L_{r-1} & \mathcal{L}_{r-1} \\ \mathcal{L}'_{r-1} & 0 & \mathcal{L}_s \end{array}\right\} \\
&= \delta_{t0}\delta_{\alpha\alpha'}\frac{[\mathcal{J}_q]}{[\mathcal{L}_{r-1},l_r]^{1/2}}\frac{[\mathcal{L}_{r-1}]^{1/2}}{[\mathcal{L}_s]^{1/2}} \\
&= \delta_{t0}\delta_{\alpha\alpha'}\frac{[\mathcal{J}_q]}{[l_s,l_r]^{1/2}} \qquad \text{(E.16)}
\end{aligned}
$$

Let us define the quantity $D'(s,r)$,

$$
D'(s,r) = (-1)^{l_r+l_s}\frac{[l_s,l_r]^{1/2}}{[\mathcal{J}_q]}D(s,r), \qquad \text{(E.17)}
$$

so that

$$
D'(1s,nl) = \delta_{t0}\delta_{\alpha\alpha'}(-1)^{l_r+l_s}. \qquad \text{(E.18)}
$$

We introduce $D'(s,r)$ to eliminate the factors $\mathcal{J}_q]$ and $(-1)^{l_r+l_s}$ from the final expression for $D_{i,i'',i'}(k_1,k_2$. For the case when subshell s is the $n'l'$ orbital and subshell r is the nl orbital we may take advantage of the relation $\mathcal{L}_{s-1}=0$ and the knowledge that there are no intervening subshells. The product series from $D_4\cdot D_4$ reduces to one. Since the subshells are singly occupied $L=L'=0$, we arrive at the following expression:

$$
\begin{aligned}
D(nl, n'l') &= \frac{[\mathcal{J}_q]}{[\mathcal{L}_r]}(-1)^{\mathcal{L}_{s-1}-\mathcal{L}_r}(-1)^{L_s+L'_s+\mathcal{L}_s-\mathcal{L}'_{r-1}+t} \\
&\quad (-1)^{l_s-l_r+L-L'}[\mathcal{L}_s, \mathcal{L}'_s]^{1/2}[\mathcal{L}_r][L_s, L'_s]^{1/2}[L_r, L'_r]^{1/2} \\
&\quad \left\{ \begin{array}{ccc} 0 & L_s & \mathcal{L}_s \\ t & \mathcal{L}'_s & L'_s \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_r & L'_r & \mathcal{L}'_s \\ t & \mathcal{L}_s & L_r \end{array} \right\} \\
&\quad \left\{ \begin{array}{ccc} 0 & l_s & L_s \\ t & L'_s & l_s \end{array} \right\} \left\{ \begin{array}{ccc} 0 & l_r & L'_r \\ t & L_r & l_r \end{array} \right\} \\
&= \delta_{L_s l_s}\delta_{L'_s l_s}\delta_{\mathcal{L}_s l_s}\delta_{\mathcal{L}'_s l_s}(-1)^{-\mathcal{L}_r+l_s-l_r+t} \\
&\quad [\mathcal{L}_r][L_r, L'_r]^{1/2} \left\{ \begin{array}{ccc} \mathcal{L}_r & L'_r & l_s \\ t & l_s & L_r \end{array} \right\} \left\{ \begin{array}{ccc} 0 & l_r & L'_r \\ t & L_r & l_r \end{array} \right\} \\
&= \delta_{\alpha\alpha'}(-1)^{-\mathcal{L}_r+l_s+l_r}[\mathcal{L}_r] \left\{ \begin{array}{ccc} \mathcal{L}_r & l_r & l_s \\ t & l_s & l_r \end{array} \right\} \qquad \text{(E.19)} \\
D'(s,r) &= \delta_{\alpha\alpha'}(-1)^{-\mathcal{L}_r}[l_s, l_r]^{1/2} \left\{ \begin{array}{ccc} \mathcal{L}_r & l_r & l_s \\ t & l_s & l_r \end{array} \right\}. \qquad \text{(E.20)}
\end{aligned}
$$

When $t = 0$, $D'(s,r)$ reduces to the solution in eq. E.18. Although the terms between the same configuration can seem complex, the matrix elements between differing configurations reduces to a very simple expressions for the configurations under consideration. We must address up to six cases to show this is true.

E.2 Transitioning Matrix Elements

For non-diagonal matrix elements of multi-electron radiators, the general transition arrays are set up so that one may calculate a matrix element where the

moving electron travels from a 'lower' subshell to a 'higher subshell'. The simplest cases to calculate are those where the relevant electron is in lower subshells in states α and α', while it is in a higher subshell in state α'', or vice versa. One cannot immediately assume the relevant lower subshells are the same. We will also address the reverse case. The most complex case is when either α or α' is in a lower subshell than α'' while the other is in a higher subshell. This is relevant, I believe, when looking at interactions between manifolds.

We will examine each factor in $D_1 \cdots D_7$ to see what simplifications can be made. Some can be simplified considerably without making all the assumptions considered. We will show six most general cases, where four of the cases shown in the schematic can be combined into two. Not including the case where $\alpha = \alpha' = \alpha''$, we have the following:

$$\textbf{Case 1}, \cdots l_i^1 l_{i'}^0 l_j^{k-1} \cdots \rightarrow \cdots l_i^0 l_{i'}^0 l_j^k \cdots \rightarrow \cdots l_i^0 l_{i'}^1 l_j^{k-1} \cdots \tag{E.21}$$

$$\textbf{Case 2}, \cdots l_i^n l_j^0 \cdots \rightarrow \cdots l_i^{n-1} l_j^1 \cdots \rightarrow \cdots l_i^n l_j^0 \cdots \tag{E.22}$$

$$\textbf{Case 3}, \cdots l_i^1 l_{i'}^0 l_m^1 l_j^0 \cdots \rightarrow \cdots l_i^0 l_{i'}^0 l_m^1 l_j^1 \cdots \rightarrow \cdots l_i^0 l_{i'}^1 l_m^1 l_j^0 \cdots \tag{E.23}$$

and

$$\textbf{Case 4}, \cdots l_i^{n-1} l_j^1 l_{j'}^0 \cdots \rightarrow \cdots l_i^n l_j^0 l_{j'}^0 \cdots \rightarrow \cdots l_i^{n-1} l_j^0 l_{j'}^1 \cdots \tag{E.24}$$

$$\textbf{Case 5}, \cdots l_i^0 l_j^k \cdots l_N \rightarrow \cdots l_i^1 l_j^{k-1} \cdots l_N \rightarrow \cdots l_i^0 l_j^k \cdots l_N \tag{E.25}$$

$$\textbf{Case 6}, \cdots l_i^0 l_m^1 l_j^1 l_{j'}^0 \cdots \rightarrow \cdots l_i^1 l_m^1 l_j^0 l_{j'}^0 \cdots \rightarrow \cdots l_i^0 l_m^1 l_j^0 l_{j'}^1 \cdots, \tag{E.26}$$

where n and k are no greater than two. There are two cases we are not considering at this time,

$$\cdots l_i^n l_j^0 \cdots \rightarrow l \cdots l_i^{n-1} l_j^1 \cdots \rightarrow \cdots l_{i'}^1 l_i^{n-1} l_j^0 \cdots, \tag{E.27}$$

and

$$\cdots l_i^0 l_j^k \cdots \rightarrow \cdots l_i^1 l_j^{k-1} \cdots l_N \rightarrow \cdots l_i^0 l_j^{k-1} l_{j'}^1 \cdots . \tag{E.28}$$

We shall show that in general $l_i = l_{i'}$ and $l_j = l_{j'}$. Therefore, if i and i' are not the same subshell, it must be a cross term between manifolds. We will not be considering such terms in this work. The first three cases above involve an electron undergoing a transition from a lower subshell to a higher one, and back down, while the second three cases involve an electron undergoing a transition from higher to lower and back. In order to calculate these terms we must remember to take the complex conjugate of one of the matrix elements, depending on which one is reversed relative to Cowan's notation.

E.3 Transition Cases 1-3

We will use D_1 as it is written in eq. C.6 and consider it on a case by case basis. We will make the same assumption that there are no more than two electrons in a given subshell so that D_2 reduces to one. The factor $D_3 \cdot D_3$ is treated in an identical manner as in section E.1 and we will use the result in eq. E.5.

We move on to D_4 and once again take advantage of the sum rules. Since the electron undergoing the transition is in the higher subshell for state α'', we can take the products in D_4 over the same subshells above j, since the upper subshell j will be the same for both matrix elements. However, we must consider the possibility that subshells j and j' are not the same in the alternate case. We now examine the first case. This process can be applied very much like the case in the previous

section, so that we arrive at the quantity,

$$\sum_{\mathcal{L}_q''} \cdots \sum_{\mathcal{L}_{j+1}''} D_4 \cdot D_4 = \frac{[\mathcal{L}_q]}{[\mathcal{L}_j]} \delta_{\mathcal{L}_j,\mathcal{L}_j'} \prod_{m=j+1}^{q} \delta_{S_m,S_m''} \delta_{S_m'',S_m'} \delta_{\mathcal{L}_m,\mathcal{L}_m'} \delta_{\alpha_m L_m S_m,\alpha_m'' L_m'' S_m''} \delta_{\alpha_m'' L_m'' S_m'',\alpha_m' L_m' S_m'} \,. \quad \text{(E.29)}$$

In order to reduce $D_5 \cdot D_5$, we must remember that we cannot assume that the relevant lower subshells l_i and l_i' are the same for the first and third cases. Let us assume that $i' \geq i$, *i.e.* the electron undergoing the transition is in a higher subshell in state α' than it is in state α. We will factor out the terms related to subshells i to i',

$$\begin{aligned} & D_5 \cdot D_5 \\ &= \left(\prod_{n=i}^{i'-1} \delta_{\alpha_n' L_n' S_n',\alpha_n'' L_n'' S_n''} \delta_{\mathcal{L}_n' S_n',\mathcal{L}_n'' S_n''} \right) (-1)^{\mathcal{L}_{i-1}+L_i''+l_i+\mathcal{L}_i} (-1)^{-\mathcal{L}_{i'-1}'-L_{i'}''-l_{i'}-\mathcal{L}_{i'}'} \\ & \quad [\mathcal{L}_i'', L_i]^{1/2} [\mathcal{L}_{i'}'', L_{i'}']^{1/2} \begin{Bmatrix} \mathcal{L}_{i-1} & L_i'' & \mathcal{L}_i'' \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix} \begin{Bmatrix} \mathcal{L}_{i'-1}' & L_{i'}'' & \mathcal{L}_{i'}'' \\ l_{i'} & \mathcal{L}_{i'}' & L_{i'}' \end{Bmatrix} \times \text{spins} \\ & \quad \left(\prod_{m=1}^{i-1} \cdots \right) . \end{aligned} \quad \text{(E.30)}$$

At this time, there are not enough common elements to simplify this expression in a way that would be useful. Like $D_5 \cdot D_5$ he product $D_6 \cdot D_6$ also does not seem to simplify at this point. We will factor out the terms in the product series that relate to subshells between i and i'.

$$D_6 \cdot D_6 = \left(\prod_{m=i+1}^{i'} \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} (-1)^{l_i + L_m + \mathcal{L}_{m-1} + \mathcal{L}''_m} \right.$$
$$\left. \times [\mathcal{L}_{m-1}, \mathcal{L}''_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}''_{m-1} & \mathcal{L}_{m-1} \\ L_m & \mathcal{L}_m & \mathcal{L}''_m \end{Bmatrix} \times \text{spins} \right) \tag{E.31}$$

$$\prod_{m=i'+1}^{j-1} \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{\alpha'_m L'_m S'_m, \alpha''_m L''_m S''_m} (-1)^{l_i + L_m + \mathcal{L}_{m-1} + \mathcal{L}''_m}$$
$$(-1)^{-l'_{i'} - L'_m - \mathcal{L}'_{m-1} - \mathcal{L}''_m} [\mathcal{L}_{m-1}, \mathcal{L}''_m]^{1/2} [\mathcal{L}'_{m-1}, \mathcal{L}''_m]^{1/2}$$
$$\begin{Bmatrix} l_i & \mathcal{L}''_{m-1} & \mathcal{L}_{m-1} \\ L_m & \mathcal{L}_m & \mathcal{L}''_m \end{Bmatrix} \begin{Bmatrix} l_{i'} & \mathcal{L}''_{m-1} & \mathcal{L}'_{m-1} \\ L'_m & \mathcal{L}'_m & \mathcal{L}''_m \end{Bmatrix} \times \text{spins}. \tag{E.32}$$

Although there may seem to be some possible points of approach to simplify $D_5 \cdot D_5$ and $D_6 \cdot D_6$, we must examine the individual cases. We finally write the formidable term D_7,

$$\begin{aligned} D_7 \cdot D_7 \;=\; & \delta_{\mathcal{S}_j, \mathcal{S}'_j} \delta_{S'_j, S''_j} (-1)^{\mathcal{S}''_{j-1} + S''_j + \mathcal{S}_j} (-1)^{-\mathcal{S}''_{j-1} - S''_j - \mathcal{S}'_j} (-1)^{L_j + l_j + L''_j} \\ & \times (-1)^{-L'_j - l'_j - L''_j} [\mathcal{S}_{j-1}, S''_j]^{1/2} [\mathcal{S}'_{j-1}, S''_j]^{1/2} \\ & [\mathcal{L}_{j-1}, L''_j, \mathcal{L}_j, \mathcal{L}''_j]^{1/2} [\mathcal{L}'_{j-1}, L''_j, \mathcal{L}'_j, \mathcal{L}''_j]^{1/2} \\ & \begin{Bmatrix} \mathcal{S}''_{j-1} & S''_j & \mathcal{S}_j \\ S_j & \mathcal{S}_{j-1} & s \end{Bmatrix} \begin{Bmatrix} \mathcal{S}''_{j-1} & S''_j & \mathcal{S}'_j \\ S'_j & \mathcal{S}'_{j-1} & s \end{Bmatrix} \\ & \begin{Bmatrix} \mathcal{L}_{j-1} & \mathcal{L}''_{j-1} & l_i \\ L_j & L''_j & l_j \\ \mathcal{L}_j & \mathcal{L}''_j & t \end{Bmatrix} \begin{Bmatrix} \mathcal{L}'_{j-1} & \mathcal{L}''_{j-1} & l_{i'} \\ L'_j & L''_j & l_j \\ \mathcal{L}'_j & \mathcal{L}''_j & t \end{Bmatrix}. \end{aligned} \tag{E.33}$$

There are a few simplifications that can be made taking advantage of the fact that $l'_j = l_j$, $\mathcal{S}_j = \mathcal{S}'_j = \mathcal{S}''_j$ and $\mathcal{S}_j = \mathcal{S}'_j$.

$$
\begin{aligned}
D_7 \cdot D_7 \;=\; & \delta_{\mathcal{S}_j,\mathcal{S}'_j}\delta_{\mathcal{S}'_j,\mathcal{S}''_j}(-1)^{L_j-L'_j}[\mathcal{S}_{j-1},\mathcal{S}'_{j-1}]^{1/2}[\mathcal{S}''_j][\mathcal{L}_{j-1},\mathcal{L}'_{j-1}]^{1/2} \\
& [L''_j,\mathcal{L}_j,\mathcal{L}''_j]\begin{Bmatrix} \mathcal{S}''_{j-1} & \mathrm{S}''_j & \mathcal{S}_j \\ \mathrm{S}_j & \mathcal{S}_{j-1} & s \end{Bmatrix}\begin{Bmatrix} \mathcal{S}''_{j-1} & \mathrm{S}''_j & \mathcal{S}_j \\ \mathrm{S}'_j & \mathcal{S}'_{j-1} & s \end{Bmatrix} \\
& \begin{Bmatrix} \mathcal{L}_{j-1} & \mathcal{L}''_{j-1} & l_i \\ L_j & L''_j & l_j \\ \mathcal{L}_j & \mathcal{L}''_j & t \end{Bmatrix}\begin{Bmatrix} \mathcal{L}'_{j-1} & \mathcal{L}''_{j-1} & l_{i'} \\ L'_j & L''_j & l_j \\ \mathcal{L}_j & \mathcal{L}''_j & t \end{Bmatrix}
\end{aligned} \tag{E.34}
$$

Before we go any further, we will remember that the jth subshell contains no more than one electron in states α and α'; this is the equivalent of $k \leq 2$. As a result, we can use the relations $L_j = L'_j$ and $\mathrm{S}_j = \mathrm{S}'_j$. We can sum over S''_j using eq. A.17 and $\mathcal{L}''_j$ and L''_j using the orthogonality relation for 9-symbols given in eq. A.20. However, we must first arrange the arguments to match eq. A.20. The Wigner 9-j symbols are multiplied by a factor of $(-1)^K$, where K is the sum of all the arguments, when exchanging a pair of columns or rows. We reduce the expression as follows:

$$
\begin{aligned}
\sum_{\mathrm{S}''_j} D_7 \cdot D_7 \;=\; & \delta_{\mathcal{S}_j,\mathcal{S}''_j}\delta_{\mathcal{S}'_{j'},\mathcal{S}''_{j'}}\delta_{\mathcal{S}_{j-1},\mathcal{S}'_{j-1}}[\mathcal{L}_{j-1},\mathcal{L}'_{j-1}]^{1/2} \times \\
& [L''_j,\mathcal{L}_j,\mathcal{L}''_j]\begin{Bmatrix} \mathcal{L}_j & t & \mathcal{L}''_j \\ L_j & l_j & L''_j \\ \mathcal{L}_{j-1} & l_i & \mathcal{L}''_{j-1} \end{Bmatrix}\begin{Bmatrix} \mathcal{L}_j & t & \mathcal{L}''_j \\ L_j & l_j & L''_j \\ \mathcal{L}'_{j-1} & l_{i'} & \mathcal{L}''_{j-1} \end{Bmatrix},
\end{aligned}
$$

$$\sum_{S''_j}\sum_{\mathcal{L}''_j,L''_j} D_7\cdot D_7 \;=\; \delta_{S_j,S''_j}\delta_{S'_{j'},S''_{j'}}\delta_{S_{j-1},S'_{j-1}}\delta_{l_i,l_{i'}}\delta_{\mathcal{L}_{j-1}\mathcal{L}'_{j-1}}\frac{[\mathcal{L}_j]}{[l_i]}. \tag{E.35}$$

This is an extraordinary result, which simplifies our calculations considerably. We also have shown that l_i equals $l_{i'}$, which indicates that α may be in the same configuration as α' or be in configurations within a Rydberg series. Let us now address the individual cases to obtain further simplifications.

E.3.1 Case 1

In the first case, we determine $D_1\cdot D_1$, knowing $n=1$ and there are no intervening subshells between i and j.

$$D_1\cdot D_1 = (-1)^{k-1-k+1}(1\cdot k) = k. \tag{E.36}$$

The product $D_2\cdot D_2$ reduces to one, $D_3\cdot D_3$ reduces to the expression in eq. E.5 and $D_4\cdot D_4$ reduces to eq. E.29. We must examine $D_5\cdot D_5$ to see if we have any simplifications. We may simplify by knowing that neither subshells i or i' are occupied in α'' so we use the following relations, $L''_i = L''_{i'} = 0$ and $l_i = l_{i'}$. We know there are no intervening subshells between i andi' so we write down the following expression:

$$\begin{aligned} D_5\cdot D_5 \;=\;& \delta_{\alpha'_i L'_i S'_i,\alpha''_i L''_i S''_i}\delta_{\mathcal{L}'_i S'_i,\mathcal{L}''_i S''_i}(-1)^{\mathcal{L}_{i-1}+\mathcal{L}_i}(-1)^{-\mathcal{L}'_{i'-1}-\mathcal{L}'_{i'}} \\ & [\mathcal{L}''_i,L_i]^{1/2}[\mathcal{L}''_i,L'_{i'}]^{1/2}\begin{Bmatrix} \mathcal{L}_{i-1} & 0 & \mathcal{L}''_i \\ l_i & \mathcal{L}_i & L_i \end{Bmatrix}\begin{Bmatrix} \mathcal{L}'_{i'-1} & 0 & \mathcal{L}''_{i'} \\ l_{i'} & \mathcal{L}'_{i'} & L'_{i'} \end{Bmatrix} \\ & \times\text{spins}\left(\prod_{m=1}^{i-1}\cdots\right), \end{aligned} \tag{E.37}$$

which simplifies to obtain the following,

$$
\begin{aligned}
D_5 \cdot D_5 &= \delta_{\alpha_i' L_i' S_i', \alpha_i'' L_i'' S_i''} \delta_{\mathcal{L}_i' S_i', \mathcal{L}_i'' S_i''} (-1)^{\mathcal{L}_{i-1}+\mathcal{L}_i} (-1)^{-\mathcal{L}'_{i'-1}-\mathcal{L}''_{i'}} [\mathcal{L}_i'', L_i]^{1/2} [\mathcal{L}_{i'}'', L_{i'}']^{1/2} \\
&\quad \delta_{\mathcal{L}_{i-1}\mathcal{L}_i''} \delta_{l_i L_i} (-1)^{\mathcal{L}_{i-1}+\mathcal{L}_i+L_i} [\mathcal{L}_{i-1}, L_i]^{-1/2} \delta_{\mathcal{L}'_{i'-1}\mathcal{L}''_{i'}} \delta_{l_{i'} L'_{i'}} \\
&\quad (-1)^{\mathcal{L}'_{i'-1}+\mathcal{L}'_{i'}+L'_{i'}} [\mathcal{L}'_{i'-1}, L'_{i'}]^{-1/2} \times \text{spins} \left(\prod_{m=1}^{i-1} \cdots \right) \\
&= \delta_{\alpha_i' L_i' S_i', \alpha_i'' L_i'' S_i''} \delta_{\mathcal{L}_i' S_i', \mathcal{L}_i'' S_i''} (-1)^{2\mathcal{L}_{i-1}+2\mathcal{L}_i+2l_i} \delta_{\mathcal{L}_{i-1}\mathcal{L}_i''} \delta_{l_i L_i} \delta_{\mathcal{L}'_{i'-1}\mathcal{L}''_{i'}} \delta_{l_{i'} L'_{i'}} \\
&\quad \times \text{spins} \left(\prod_{m=1}^{i-1} \cdots \right) \\
&= \delta_{\alpha_i' L_i' S_i', \alpha_i'' L_i'' S_i''} \delta_{\mathcal{L}_i' S_i', \mathcal{L}_i'' S_i''} \delta_{\mathcal{L}_{i-1}\mathcal{L}_i''} \delta_{l_i L_i} \delta_{\mathcal{L}'_{i'-1}\mathcal{L}''_{i'}} \delta_{l_{i'} L'_{i'}} \\
&\quad \times \text{spins} \left(\prod_{m=1}^{i-1} \cdots \right). \qquad \text{(E.38)}
\end{aligned}
$$

We remember that $\mathcal{L}_{i-1}$, $\mathcal{L}_i$, and $L_i = l_i$ satisfy a triangle relation so the quantity -1^{2K} where K equals the sum of these arguments, drops out. Although all these quantities are integers, the corresponding spin values may not be.

When evaluating $D_6 \cdot D_6$, we remember that there are no intervening subshells between i' and j so that the second product series reduces to one, also, i' is unoccupied in state α, so $L_{i'} = 0$. The product $D_6 \cdot D_6$ reduces as follows:

$$
\begin{aligned}
D_6 \cdot D_6 &= \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha_{i'}'' L_{i'}'' S_{i'}''} (-1)^{l_i+\mathcal{L}_{i'-1}+\mathcal{L}_{i'}''} [\mathcal{L}_{i'-1}, \mathcal{L}_{i'}'']^{1/2} \\
&\quad \begin{Bmatrix} l_i & \mathcal{L}_{i'-1}'' & \mathcal{L}_{i'-1} \\ 0 & \mathcal{L}_{i'} & \mathcal{L}_{i'}'' \end{Bmatrix} \times \text{spins} \\
&= \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha_{i'}'' L_{i'}'' S_{i'}''} (-1)^{l_i+\mathcal{L}_i+\mathcal{L}_{i'}''} [\mathcal{L}_i, \mathcal{L}_{i'}'']^{1/2} \\
&\quad \delta_{\mathcal{L}_i'' \mathcal{L}_{i'}''} \delta_{\mathcal{L}_i \mathcal{L}_{i'}} (-1)^{l_i+\mathcal{L}_i''+\mathcal{L}_i} [\mathcal{L}_i'', \mathcal{L}_i]^{-1/2} \times \text{spins}, \qquad \text{(E.39)}
\end{aligned}
$$

which simplifies to obtain the following,

$$D_6 \cdot D_6 \;=\; \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha''_{i'} L''_{i'} S''_{i'}} \delta_{\mathcal{L}''_{i'} \mathcal{L}''_{i'}} \delta_{\mathcal{L}_i \mathcal{L}_{i'}} \times \text{spins} \tag{E.40}$$

Now we may combine $D_1 \cdot D_1$ through $D_7 \cdot D_7$,

$$\begin{aligned}
&\sum_{\mathcal{J}''} \sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{j+1}} \sum_{S''_j} \sum_{\mathcal{L}''_j, L''_j} D \cdot D \\
&= \; k \cdot \frac{[\mathcal{J}_q]}{[\mathcal{L}_q]} \frac{[\mathcal{L}_q]}{[\mathcal{L}_j]} \frac{[\mathcal{L}_j]}{[l_i]} \delta_{\mathcal{L}_j, \mathcal{L}'_j} \delta_{S_q, S''_q} \delta_{S''_q, S'_q} \delta_{\alpha'_i L'_i S'_i, \alpha''_i L''_i S''_i} \delta_{\mathcal{L}'_i S'_i, \mathcal{L}''_i S''_i} \\
&\quad \delta_{\mathcal{L}_{i-1} \mathcal{L}''_i} \delta_{l_i L_i} \delta_{\mathcal{L}'_{i'-1}, \mathcal{L}''_{i'}} \delta_{l_{i'} L'_{i'}} \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha''_{i'} L''_{i'} S''_{i'}} \delta_{\mathcal{L}''_{i'} \mathcal{L}''_{i'}} \delta_{\mathcal{L}_i \mathcal{L}_{i'}} \times \text{spins} \\
&\quad \delta_{S_j, S''_{j'}} \delta_{S'_{j'}, S''_{j'}} \delta_{S_{j-1}, S'_{j-1}} \delta_{l_i l_{i'}} \delta_{\mathcal{L}_{j-1} \mathcal{L}'_{j-1}} \prod_{m=j+1}^{q} \delta_{S_m, S''_m} \delta_{S''_m, S'_m} \\
&\quad \delta_{\mathcal{L}_m, \mathcal{L}'_m} \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{\alpha'_m L'_m S'_m, \alpha''_m L''_m S''_m} \left(\prod_{m=1}^{i-1} \cdots \right) \\
&= \; k \cdot \frac{[\mathcal{J}_q]}{[l_i]} \delta_{\alpha\alpha'}.
\end{aligned} \tag{E.41}$$

This reduces to a very simple result. In fact, we will show that for "near-hydrogenic" cases, where $w_m = 0$ and $n = k = 1$, it reduces to the hydrogenic result of Woltz [13, 14].

E.3.2 Case 2

As in the first case, we determine $D_1 \cdot D_1$, knowing $k = 1$ and there are no intervening subshells between i and j,

$$D_1 \cdot D_1 = (n \cdot 1) = n. \tag{E.42}$$

The product $D_2 \cdot D_2$ reduces to one, $D_3 \cdot D_3$ reduces to the expression in eq. E.5 and $D_4 \cdot D_4$ still reduces to eq. E.29. As we examine $D_5 \cdot D_5$ in eq. E.30, we remember $i = i'$ so the first product series in drops out. Within the second product series we employ the relation $\mathcal{L}_{i-1} = \mathcal{L}''_{i-1} = \mathcal{L}'_{i-1}$ to simplify the following expression:

$$\begin{aligned} D_5 \cdot D_5 &= (-1)^{\mathcal{L}_i - \mathcal{L}'_i} [\mathcal{L}''_i, L_i]^{1/2} [\mathcal{L}''_i, L'_i]^{1/2} \\ &\quad \left\{ \begin{array}{ccc} \mathcal{L}_{i-1} & L''_i & \mathcal{L}''_i \\ l_i & \mathcal{L}_i & L_i \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_{i-1} & L''_i & \mathcal{L}''_i \\ l_i & \mathcal{L}'_i & L'_i \end{array} \right\} \\ &\quad \times \text{spins} \left(\prod_{m=1}^{i-1} \cdots \right). \end{aligned} \tag{E.43}$$

We seem at an impasse, however, from eq. E.34, we have the relations $\mathcal{L}_{j-1} = \mathcal{L}'_{j-1}$ and $j - 1 = i$,

$$\sum_{\mathcal{L}''_i} D_5 \cdot D_5 = \delta_{L_i L'_i} \delta_{s_i S'_i} \left(\prod_{m=1}^{i-1} \cdots \right). \tag{E.44}$$

As in the first case $D_6 \cdot D_6$ reduces to one, and $D_7 \cdot D_7$ is obtained from eq. E.34. Combining our results, we get a result very similar to the first case,

$$\begin{aligned} &\sum_{\mathcal{J}''} \sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{j+1}} \sum_{S''_j} \sum_{\mathcal{L}''_j, L''_j} \sum_{\mathcal{L}''_i} D \cdot D \\ &\quad = n \frac{[\mathcal{J}_q]}{[l_i]} \delta_{L_i L_{i'}} \delta_{\alpha\alpha'}. \end{aligned} \tag{E.45}$$

E.3.3 Case 3

This case is very similar to the first case, however there is an intervening occupied subshell m. It will make itself apparent in the quantity, $D_6 \cdot D_6$. We first obtain an expression for $D_1 \cdot D_1$,

$$D_1 \cdot D_1 = (-1)^{1-1}(n \cdot k) = 1. \tag{E.46}$$

The product $D_2 \cdot D_2$ reduces to one, $D_3 \cdot D_3$ reduces to the expression in eq. E.5 and $D_4 \cdot D_4$ still reduces to eq. E.29. We can use our result for the first case for $D_5 \cdot D_5$ in eq. E.38. We now examine $D_6 \cdot D_6$. Since subshell m is singly occupied we may use the relation $L_m = L'_m = L''_m = l_m$. Also, as in the first case, subshell i' is unoccupied in state α so we use the relation, $L_{i'} = 0$, to obtain the following expression:

$$\begin{aligned} D_6 \cdot D_6 \;=\; & \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha''_{i'} L''_{i'} S''_{i'}} (-1)^{l_i + \mathcal{L}_i + \mathcal{L}''_{i'}} [\mathcal{L}_i, \mathcal{L}''_{i'}]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}''_i & \mathcal{L}_i \\ 0 & \mathcal{L}_{i'} & \mathcal{L}''_{i'} \end{Bmatrix} \times \text{spins} \\ & \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{\alpha'_m L'_m S'_m, \alpha''_m L''_m S''_m} (-1)^{\mathcal{L}_{i'} - \mathcal{L}'_{i'}} \\ & [\mathcal{L}_{i'}, \mathcal{L}''_m]^{1/2} [\mathcal{L}'_{i'}, \mathcal{L}''_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}''_{i'} & \mathcal{L}_{i'} \\ l_m & \mathcal{L}_m & \mathcal{L}''_m \end{Bmatrix} \begin{Bmatrix} l_i & \mathcal{L}''_{i'} & \mathcal{L}'_{i'} \\ l_m & \mathcal{L}'_m & \mathcal{L}''_m \end{Bmatrix} \\ & \times \text{spins}. \end{aligned} \tag{E.47}$$

The first 6-j symbol with drop out as it did in Case 1, but we need to use the relation that $\mathcal{L}_{j-1} = \mathcal{L}'_{j-1}$ where $j - 1 = m$,

$$
\begin{aligned}
D_6 \cdot D_6 \;=\; & \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha''_{i'} L''_{i'} S''_{i'}} \delta_{\mathcal{L}''_i \mathcal{L}''_{i'}} \delta_{\mathcal{L}_{i'} \mathcal{L}_i} \times \text{spins} \\
& \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{\alpha'_m L'_m S'_m, \alpha''_m L''_m S''_m} \\
& (-1)^{\mathcal{L}_{i'} - \mathcal{L}'_{i'}} [\mathcal{L}_{i'}, \mathcal{L}''_m]^{1/2} [\mathcal{L}'_{i'}, \mathcal{L}''_m]^{1/2} \\
& \left\{ \begin{array}{ccc} l_i & \mathcal{L}''_{i'} & \mathcal{L}_{i'} \\ l_m & \mathcal{L}_m & \mathcal{L}''_m \end{array} \right\} \left\{ \begin{array}{ccc} l_i & \mathcal{L}''_{i'} & \mathcal{L}'_{i'} \\ l_m & \mathcal{L}_m & \mathcal{L}''_m \end{array} \right\} \times \text{spins} \\
\sum_{\mathcal{L}''_m} D_6 \cdot D_6 \;=\; & \delta_{\alpha_{i'} L_{i'} S_{i'}, \alpha''_{i'} L''_{i'} S''_{i'}} \delta_{\mathcal{L}''_i \mathcal{L}''_{i'}} \delta_{\mathcal{L}_{i'} \mathcal{L}_i} \times \text{spins} \\
& \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{\alpha'_m L'_m S'_m, \alpha''_m L''_m S''_m} \delta_{\mathcal{L}_{i'} \mathcal{L}'_{i'}} \times \text{spins}. \qquad \text{(E.48)}
\end{aligned}
$$

Combining our results, using eq. E.34, we once again get a result very similar to the first case,

$$
\sum_{\mathcal{J}''} \sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{j+1}} \sum_{S''_j} \sum_{\mathcal{L}''_j, L''_j} \sum_{\mathcal{L}''_m} D \cdot D = \frac{[\mathcal{J}_q]}{[l_i]} \delta_{\alpha\alpha'}. \qquad \text{(E.49)}
$$

At this point, the author finds it quite amazing that result reduces to something so simple. This allows one to write a code for simple multi-electron cases without keeping accounts of all the intermediate angular sums.

E.4 Transition Cases 4-6

In these cases, it is the electron in the jth subshell that is undergoing a transition. We find the result for $D_4 \cdot D_4$ somewhat more complex because we may not always assume j equals j'. Let us rewrite $D_4 \cdot D_4$ with that understanding,

$$D_4 \cdot D_4 = \prod_{m=j+1}^{q} \prod_{n=j'+1}^{q} \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{S_m, S''_m} \delta_{\alpha''_n L''_n S''_n, \alpha'_n L'_n S'_n} \delta_{S''_n, S'_n}$$
$$(-1)^{-\mathcal{L}''_{m-1} - L''_m - \mathcal{L}_m - t} (-1)^{\mathcal{L}''_{n-1} + L''_n + \mathcal{L}'_n + t} [\mathcal{L}''_m, \mathcal{L}_m]^{1/2} [\mathcal{L}'_n, \mathcal{L}''_n]^{1/2}$$
$$\left\{ \begin{array}{ccc} \mathcal{L}''_{m-1} & L''_m & \mathcal{L}''_m \\ \mathcal{L}_m & t & \mathcal{L}_{m-1} \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}''_{n-1} & L''_n & \mathcal{L}''_n \\ \mathcal{L}'_n & t & \mathcal{L}'_{n-1} \end{array} \right\}. \qquad \text{(E.50)}$$

As one can see, the order is different as in the first three cases, because we must keep track of the matrix elements in which the transitioning electron moves from a lower subshell to a higher subshell, or vice versa. Once again, we can use the relationship from eq E.5, $\mathcal{L}_q = \mathcal{L}'_q$, to reduce the previous expression in the same manner as in section E.3 up to subshell j',

$$\sum_{\mathcal{L}''_q \cdots \mathcal{L}''_{j'+1}} D_4 \cdot D_4 = \delta_{\alpha_{j'} L_{j'} S_{j'}, \alpha''_{j'} L''_{j'} S''_{j'}} \delta_{S_{j'}, S''_{j'}} \delta_{\mathcal{L}_{j'}, \mathcal{L}'_{j'}} \frac{[\mathcal{L}_q]}{[\mathcal{L}_{j'}]}$$
$$(-1)^{-\mathcal{L}''_j - L''_{j'} - \mathcal{L}_{j'} - t} [\mathcal{L}_{j'}, \mathcal{L}''_{j'}]^{1/2} \left\{ \begin{array}{ccc} \mathcal{L}''_j & L''_{j'} & \mathcal{L}''_{j'} \\ \mathcal{L}_{j'} & t & \mathcal{L}_j \end{array} \right\}$$
$$\prod_{m=j'+1}^{q} \delta_{\alpha_m L_m S_m, \alpha''_m L''_m S''_m} \delta_{S_m, S''_m} \delta_{\alpha''_m L''_m S''_m, \alpha'_m L'_m S'_m} \delta_{S''_m, S'_m}. \qquad \text{(E.51)}$$

We cannot simplify this further until we examine specific cases.

As we examine $D_5 \cdot D_5$, we may use the fact that subshell i and i' are the same,

$$
\begin{aligned}
D_5 \cdot D_5 \;=\; & \left(\prod_{m=1}^{i-1} \delta_{\alpha_m L_m \mathrm{S}_m, \alpha''_m L''_m \mathrm{S}''_m} \delta_{\alpha''_m L''_m \mathrm{S}''_m, \alpha'_m L'_m \mathrm{S}'_m} \delta_{\mathcal{L}_m \mathcal{S}_m, \mathcal{L}''_m \mathcal{S}''_m} \delta_{\mathcal{L}''_m \mathcal{S}''_m, \mathcal{L}'_m \mathcal{S}'_m} \right) \\
& (-1)^{-\mathcal{L}''_{i-1} - L_i - l_i - \mathcal{L}''_i} (-1)^{\mathcal{L}''_{i-1} + L'_i + l_i + \mathcal{L}''_i} [\mathcal{L}_i, L''_i]^{1/2} [\mathcal{L}'_i, L''_i]^{1/2} \\
& \left\{ \begin{array}{ccc} \mathcal{L}''_{i-1} & L_i & \mathcal{L}_i \\ l_i & \mathcal{L}''_i & L''_i \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}''_{i-1} & L'_i & \mathcal{L}'_i \\ l_i & \mathcal{L}''_i & L''_i \end{array} \right\} \times \text{spins.}
\end{aligned} \tag{E.52}
$$

Here we can make a useful assumption, that the occupancy of the ith subshell is no more than one in states α and α', which is equivalent to saying $n = n' \leq 2$. We may use the relations, $L_i = L'_i = 0$ if $n = 0$ and $L_i = L'_i = l_i$ if $n = 1$, to sum over L''_i and S''_i. We obtain the following expression:

$$
\sum_{L''_i} \sum_{\mathrm{S}''_i} D_5 \cdot D_5 \;=\; \left(\prod_{m=1}^{i-1} \cdots \right) \delta_{\mathcal{L}_i \mathcal{L}'_i} \delta_{\mathcal{S}_i \mathcal{S}'_i}, \qquad n \leq 2. \tag{E.53}
$$

In order to simplify $D_6 \cdot D_6$ and $D_7 \cdot D_7$, we must examine individual cases.

E.4.1 Case 4

Once again we calculate $D_1 \cdot D_1$,

$$
D_1 = (-1)^0 (n) = n. \tag{E.54}
$$

The product $D_2 \cdot D_2$ reduces to one, $D_3 \cdot D_3$ reduces to the expression in eq. E.5 and $D_5 \cdot D_5$ reduces to eq. E.53. However, we must make some simplifications to $D_4 \cdot D_4$. We know that subshell j' is unoccupied in state α'', so we may use the

relation, $\mathcal{L}''_{j'} = 0$ in eq. E.51,

$$\begin{aligned}
\sum_{\mathcal{L}''_q \cdots \mathcal{L}''_{j'+1}} D_4 \cdot D_4 &= \delta_{\alpha_{j'} L_{j'} S_{j'}, \alpha''_{j'} L''_{j'} S''_{j'}} \delta_{S_{j'}, S''_{j'}} \delta_{\mathcal{L}_{j'}, \mathcal{L}'_{j'}} \frac{[\mathcal{L}_q]}{[\mathcal{L}_{j'}]} (-1)^{-\mathcal{L}''_j - \mathcal{L}_{j'} - t} \\
&\quad [\mathcal{L}_{j'}, \mathcal{L}''_{j'}]^{1/2} \left\{ \begin{array}{ccc} \mathcal{L}''_j & 0 & \mathcal{L}''_{j'} \\ \mathcal{L}_{j'} & t & \mathcal{L}_j \end{array} \right\} \prod_{m=j'+1}^{q} \cdots \\
&= \delta_{\alpha_{j'} L_{j'} S_{j'}, \alpha''_{j'} L''_{j'} S''_{j'}} \delta_{S_{j'}, S''_{j'}} \delta_{\mathcal{L}_j, \mathcal{L}'_{j'}} \delta_{\mathcal{L}_{j'}, \mathcal{L}_j} \delta_{\mathcal{L}'_j, \mathcal{L}''_{j'}} \frac{[\mathcal{L}_q]}{[\mathcal{L}_{j'}]} \\
&\quad \times \prod_{m=j'+1}^{q} (\cdots) . \qquad \text{(E.55)}
\end{aligned}$$

We now examine $D_6 \cdot D_6$, since $D_5 \cdots D_5$ is completely simplified. We note that there are no occupied intervening subshells between subshells i and j or between j and j'. We remember that subshell j is unoccupied in state α'' so $L''_j = 0$,

$$\begin{aligned}
D_6 \cdot D_6 &= \delta_{\alpha'_j L'_j S'_j, \alpha''_j L''_j S''_j} (-1)^{l_i + L''_j + \mathcal{L}''_i + \mathcal{L}'_j} \\
&\quad [\mathcal{L}''_i, \mathcal{L}'_j]^{1/2} \left\{ \begin{array}{ccc} l_i & \mathcal{L}'_i & \mathcal{L}''_i \\ L''_j & \mathcal{L}''_j & \mathcal{L}'_j \end{array} \right\} \times \text{spins} \\
&= \delta_{\alpha'_j L'_j S'_j, \alpha''_j L''_j S''_j} \delta_{\mathcal{L}'_i \mathcal{L}'_j} \delta_{\mathcal{L}''_j \mathcal{L}''_i} \times \text{spins}. \qquad \text{(E.56)}
\end{aligned}$$

Returning to $D_7 \cdot D_7$, this product does not simplify as easily as in the first three cases. We begin by writing out the full expression:

$$
\begin{aligned}
D_7 \cdot D_7 \;=\;& \delta_{\mathcal{S}_j,\mathcal{S}''_j}\delta_{\mathcal{S}'_{j'},\mathcal{S}''_{j'}}(-1)^{-\mathcal{S}_{j-1}-\mathrm{S}_j-\mathcal{S}''_j}(-1)^{\mathcal{S}'_{j'-1}+\mathcal{S}'_{j'}+\mathcal{S}''_{j'}} \\
& (-1)^{-L''_j-l_j-L_j}(-1)^{L''_{j'}+l_{j'}+L'_{j'}}[\mathcal{S}''_{j-1},\mathrm{S}_j]^{1/2}[\mathcal{S}''_{j'-1},\mathrm{S}'_{j'}]^{1/2} \\
& [\mathcal{L}''_{j-1},L_j,\mathcal{L}''_j,\mathcal{L}_j]^{1/2}[\mathcal{L}''_{j'-1},L'_{j'},\mathcal{L}''_{j'},\mathcal{L}_{j'}]^{1/2} \\
& \left\{\begin{array}{ccc} \mathcal{S}_{j-1} & \mathrm{S}_j & \mathcal{S}''_j \\ \mathrm{S}''_j & \mathcal{S}''_{j-1} & s \end{array}\right\}\left\{\begin{array}{ccc} \mathcal{S}'_{j'-1} & \mathrm{S}'_{j'} & \mathcal{S}''_{j'} \\ \mathrm{S}''_{j'} & \mathcal{S}''_{j'-1} & s \end{array}\right\} \\
& \left\{\begin{array}{ccc} \mathcal{L}''_{j-1} & \mathcal{L}_{j-1} & l_i \\ L''_j & L_j & l_j \\ \mathcal{L}''_j & \mathcal{L}_j & t \end{array}\right\}\left\{\begin{array}{ccc} \mathcal{L}''_{j'-1} & \mathcal{L}'_{j'-1} & l_i \\ L''_{j'} & L'_{j'} & l_{j'} \\ \mathcal{L}''_{j'} & \mathcal{L}'_{j'} & t \end{array}\right\}. \qquad \text{(E.57)}
\end{aligned}
$$

For this case we will remember that subshells j and j' are unoccupied in state α'', so we may use the relations, $\mathrm{S}''_j = \mathrm{S}''_{j'} = L''_j = L''_{j'} = 0$,

$$
\begin{aligned}
D_7 \cdot D_7 \;=\;& \delta_{\mathcal{S}_j,\mathcal{S}''_j}\delta_{\mathcal{S}'_{j'},\mathcal{S}''_{j'}}(-1)^{-\mathcal{S}_i-\mathrm{S}_j-\mathcal{S}''_j}(-1)^{\mathcal{S}'_{j'}+\mathrm{S}'_{j'}+\mathcal{S}''_{j'}} \\
& (-1)^{-L''_j-l_j-L_j+L''_{j'}+l_{j'}+L'_{j'}}[\mathcal{S}''_i,\mathrm{S}_j]^{1/2}[\mathcal{S}''_j,\mathrm{S}'_{j'}]^{1/2} \\
& [\mathcal{L}''_i,L_j,\mathcal{L}''_j,\mathcal{L}_j]^{1/2}[\mathcal{L}''_j,L'_{j'},\mathcal{L}''_{j'},\mathcal{L}'_{j'}]^{1/2} \\
& \left\{\begin{array}{ccc} \mathcal{S}_i & \mathrm{S}_j & \mathcal{S}''_j \\ 0 & \mathcal{S}''_{j-1} & s \end{array}\right\}\left\{\begin{array}{ccc} \mathcal{S}'_{j'-1} & \mathrm{S}'_{j'} & \mathcal{S}''_{j'} \\ 0 & \mathcal{S}''_{j'-1} & s \end{array}\right\} \\
& \left\{\begin{array}{ccc} \mathcal{L}''_i & \mathcal{L}_{j-1} & l_i \\ 0 & L_j & l_j \\ \mathcal{L}''_j & \mathcal{L}_j & t \end{array}\right\}\left\{\begin{array}{ccc} \mathcal{L}''_j & \mathcal{L}'_{j'-1} & l_i \\ 0 & L'_{j'} & l_{j'} \\ \mathcal{L}''_{j'} & \mathcal{L}'_{j'} & t \end{array}\right\}. \qquad \text{(E.58)}
\end{aligned}
$$

Since arguments in a column or row of a 9-j symbol must obey a triangle relation, $L'_{j'} = l_{j'}$, $L_j = l_j$, and $\mathcal{L}''_i = \mathcal{L}''_j = \mathcal{L}''_{j'}$. By employing eq. A.19 and A.22, we get the following expression:

$$
\begin{aligned}
D_7 \cdot D_7 &= \delta_{S_j,S''_j}\delta_{S'_{j'},S''_{j'}}\delta_{S_{j'}s}\delta_{S''_{j'}S''_i}\delta_{S'_{j'}s}\delta_{S''_{j'},S''_j} \\
&\quad (-1)^{L''_{j'}-L''_j}[\mathcal{L}''_i, L_j, \mathcal{L}''_j, \mathcal{L}_j]^{1/2}[\mathcal{L}''_j, L'_{j'}, \mathcal{L}''_{j'}, \mathcal{L}_{j'}]^{1/2} \\
&\quad \left\{ \begin{array}{ccc} \mathcal{L}_j & t & \mathcal{L}''_j \\ \mathcal{L}_i & l_i & \mathcal{L}''_i \\ l_j & l_j & 0 \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}'_{j'} & t & \mathcal{L}''_{j'} \\ \mathcal{L}'_{j'-1} & l_i & \mathcal{L}''_j \\ j' & l_{j'} & 0 \end{array} \right\} \\
D_7 \cdot D_7 &= \delta_{S_j,S''_j}\delta_{S'_{j'},S''_{j'}}[\mathcal{L}''_j, \mathcal{L}_j]^{1/2}[\mathcal{L}''_{j'}, \mathcal{L}_{j'}]^{1/2} \\
&\quad \delta_{S_{j'}s}\delta_{S''_{j'}S''_i}\delta_{S'_{j'},s}\delta_{S''_{j'}S''_j}\delta_{L'_{j'},l_{j'}}\delta_{L_jl_j}\delta_{\mathcal{L}''_j\mathcal{L}''_i}\delta_{\mathcal{L}''_j\mathcal{L}''_{j'}} \\
&\quad (-1)^{\mathcal{L}_i+l_j+\mathcal{L}'_{j'}+l_{j'}} \\
&\quad \left\{ \begin{array}{ccc} \mathcal{L}_j & t & \mathcal{L}''_j \\ l_i & \mathcal{L}_i & l_j \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}'_{j'} & t & \mathcal{L}''_j \\ l_i & \mathcal{L}'_j & l_{j'} \end{array} \right\}.
\end{aligned} \tag{E.59}
$$

We will employ some of the relations discovered previously, $\mathcal{L}_j = \mathcal{L}_{j'} = \mathcal{L}'_{j'}$ and $\mathcal{L}_i = \mathcal{L}'_i = \mathcal{L}'_j$,

$$
\begin{aligned}
D_7 \cdot D_7 &= \delta_{S_j,S''_j}\delta_{S'_{j'},S''_{j'}}[\mathcal{L}''_j, \mathcal{L}_j]^{1/2}[\mathcal{L}''_{j'}, \mathcal{L}_j]^{1/2} \\
&\quad \delta_{S_{j'}s}\delta_{S''_jS''_i}\delta_{S'_{j'},s}\delta_{S''_{j'}S''_j}\delta_{L'_{j'},l_{j'}}\delta_{L_jl_j}\delta_{\mathcal{L}''_j\mathcal{L}''_i}\delta_{\mathcal{L}''_j\mathcal{L}''_{j'}} \\
&\quad (-1)^{l_j+l_{j'}} \left\{ \begin{array}{ccc} \mathcal{L}_j & t & \mathcal{L}''_j \\ l_i & \mathcal{L}_i & l_j \end{array} \right\} \left\{ \begin{array}{ccc} \mathcal{L}_j & t & \mathcal{L}''_j \\ l_i & \mathcal{L}_i & l_{j'} \end{array} \right\} \\
\sum_{\mathcal{L}''_j} D_7 \cdot D_7 &= \frac{[\mathcal{L}_j]^{1/2}}{[l_j]^{1/2}}(\delta_{l_jl_{j'}} \cdots).
\end{aligned} \tag{E.60}
$$

Once again, the product $D_7 \cdot D_7$ reduces down to a simple solution; however, there is a factor of $(2l_j + 1)$ in the denominator, rather than $(2l_i + 1)$. This factor is dependent on the orbital angular momentum of the electron undergoing the transition when it is in state α and α', which is consistent with the first three cases. We now obtain an expression for the entire product,

$$\sum_{\mathcal{J}''} \sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{j'}} D \cdot D \;=\; n \frac{[\mathcal{J}_q]}{[l_j]} \delta\alpha\alpha'. \tag{E.61}$$

E.4.2 Case 5

First, we calculate $D_1 \cdot D_1$,

$$D_1 \cdot D_1 = (-1)^{k-1-k+1}(n \cdot k) = k \tag{E.62}$$

The product $D_2 \cdot D_2$ reduces to one, $D_3 \cdot D_3$ reduces to the expression in eq. E.5 and $D_5 \cdot D_5$ reduces to eq. E.53. Since $j = j'$, we may use the solution for the first three cases for $D_4 \cdot D_4$ in eq. E.29. The product $D_6 \cdot D_6$ reduces to one because there are no occupied subshells between i and j. This leaves us with $D_7 \cdot D_7$. We can use the relation $\mathcal{L}_j = \mathcal{L}'_j$ from $D_4 \cdot D_4$, and $\mathcal{L}_i = \mathcal{L}'_i$ and $\mathcal{S}_i = \mathcal{S}'_i$ from $D_5 \cdot D_5$ to obtain the following expression:

$$
\begin{aligned}
D_7 \cdot D_7 &= \delta_{S_j,S_j''}\delta_{S_j',S_j''}(-1)^{S_j'-S_j}(-1)^{L_j'-L_j}[\mathcal{S}_i'',\mathrm{S}_j][\mathcal{S}_i'',\mathrm{S}_{j'}']^{1/2}[\mathcal{S}_i'',\mathrm{S}_{j'}']^{1/2} \\
&\quad [\mathcal{L}_i'',\mathcal{L}_j'',\mathcal{L}_j][L_j,L_j']^{1/2} \\
&\quad \begin{Bmatrix} \mathcal{S}_i & \mathrm{S}_j & \mathcal{S}_j'' \\ \mathrm{S}_j'' & \mathcal{S}_i'' & s \end{Bmatrix} \begin{Bmatrix} \mathcal{S}_i & \mathrm{S}_j' & \mathcal{S}_j'' \\ \mathrm{S}_j'' & \mathcal{S}_i'' & s \end{Bmatrix} \\
&\quad \begin{Bmatrix} \mathcal{L}_i'' & \mathcal{L}_i & l_i \\ L_j'' & L_j & l_j \\ \mathcal{L}_j'' & \mathcal{L}_j & t \end{Bmatrix} \begin{Bmatrix} \mathcal{L}_i'' & \mathcal{L}_i & l_i \\ L_j'' & L_j' & l_j \\ \mathcal{L}_j'' & \mathcal{L}_j & t \end{Bmatrix} \\
\sum_{\mathcal{S}_i''} D_7 \cdot D_7 &= \delta_{S_j,S_j''}\delta_{S_j',S_j''}(-1)^{L_j'-L_j} \\
&\quad [\mathcal{L}_i'',\mathcal{L}_j'',\mathcal{L}_j][L_j,L_j']^{1/2}\delta_{S_jS_j'} \\
&\quad \begin{Bmatrix} \mathcal{L}_j & t & \mathcal{L}_j'' \\ \mathcal{L}_i & l_i & \mathcal{L}_i'' \\ L_j & l_j & L_j'' \end{Bmatrix} \begin{Bmatrix} \mathcal{L}_j & t & \mathcal{L}_j'' \\ \mathcal{L}_i & l_i & \mathcal{L}_i'' \\ L_j' & l_j & L_j'' \end{Bmatrix} \\
\sum_{\mathcal{L}_i''}\sum_{\mathcal{L}_j''}\sum_{\mathcal{S}_i''} D_7 \cdot D_7 &= \frac{[\mathcal{L}_j]}{[l_j]}\delta_{S_j,S_j''}\delta_{S_j',S_j''}\delta_{L_jL_j}\delta_{S_jS_j'}. \qquad \text{(E.63)}
\end{aligned}
$$

We obtain the same solution as Case 4, shown in eq. E.61, barring $D_1 \cdot D_1$.

$$
\sum_{\mathcal{J}''}\sum_{\mathcal{L}_q''}\cdots\sum_{\mathcal{L}_{j'}''} D \cdot D = k\frac{[\mathcal{J}_q]}{[l_j]}\delta\alpha\alpha'. \qquad \text{(E.64)}
$$

E.4.3 Case 6

For this case, the product $D_2 \cdot D_2$ reduces to one, $D_3 \cdot D_3$ reduces to the expression in eq. E.5 and $D_5 \cdot D_5$ reduces to eq. E.53. The product $D_4 \cdot D_4$ reduces

to the result for case 4, in eq. E.55 The only difference between this and case 4 is that there is an intervening occupied subshell. We first obtain and expression for $D_1 \cdot D_1$,

$$D_1 \cdot D_1 = (-1)^{1-1}(n \cdot k) = 1. \tag{E.65}$$

We then examine $D_6 \cdot D_6$ by writing down the full expression,

$$\begin{aligned} D_6 \cdot D_6 \;=\; & \prod_{m=i+1}^{j-1} \delta_{\alpha''_m L''_m \mathrm{S}''_m, \alpha_m L_m \mathrm{S}_m} (-1)^{-l_i - L''_m - \mathcal{L}''_{m-1} - \mathcal{L}_m} \\ & \times [\mathcal{L}''_{m-1}, \mathcal{L}_m]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}_{m-1} & \mathcal{L}''_{m-1} \\ L''_m & \mathcal{L}''_m & \mathcal{L}_m \end{Bmatrix} \times \text{spins} \\ & \times \prod_{n=i+1}^{j'-1} \delta_{\alpha''_n L''_n \mathrm{S}''_n, \alpha'_n L'_n \mathrm{S}'_n} (-1)^{l_i + L''_n + \mathcal{L}''_{n-1} + \mathcal{L}'_n} \\ & \times [\mathcal{L}''_{n-1}, \mathcal{L}'_n]^{1/2} \begin{Bmatrix} l_i & \mathcal{L}'_{n-1} & \mathcal{L}''_{n-1} \\ L''_n & \mathcal{L}''_n & \mathcal{L}'_n \end{Bmatrix} \times \text{spins}. \end{aligned} \tag{E.66}$$

We rearrange the terms, factoring out the term relevant to subshell j, and remember that subshell is unoccupied for state α'', so we may use the relation $L''_j = 0$,

$$\begin{aligned} D_6 \cdot D_6 \;=\; & \delta_{\alpha''_j L''_j \mathrm{S}''_j, \alpha'_j L'_j \mathrm{S}'_j} (-1)^{l_i + L''_j + \mathcal{L}''_{j-1} + \mathcal{L}'_j} \times [\mathcal{L}''_{j-1}, \mathcal{L}'_j]^{1/2} \\ & \begin{Bmatrix} l_i & \mathcal{L}'_{j-1} & \mathcal{L}''_{j-1} \\ 0 & \mathcal{L}''_j & \mathcal{L}'_j \end{Bmatrix} \times \text{spins} \\ & \delta_{\alpha''_m L''_m \mathrm{S}''_m, \alpha_m L_m \mathrm{S}_m} \delta_{\alpha''_m L''_m \mathrm{S}''_m, \alpha'_m L'_m \mathrm{S}'_m} (-1)^{-l_i - L''_m - \mathcal{L}''_{m-1} - \mathcal{L}_m} \\ & (-1)^{l_i + L''_m + \mathcal{L}''_{m-1} + \mathcal{L}'_m} [\mathcal{L}''_{m-1}, \mathcal{L}_m]^{1/2} [\mathcal{L}''_{m-1}, \mathcal{L}'_m]^{1/2} \\ & \begin{Bmatrix} l_i & \mathcal{L}_{m-1} & \mathcal{L}''_{m-1} \\ L''_m & \mathcal{L}''_m & \mathcal{L}_m \end{Bmatrix} \begin{Bmatrix} l_i & \mathcal{L}'_{m-1} & \mathcal{L}''_{m-1} \\ L''_m & \mathcal{L}''_m & \mathcal{L}'_m \end{Bmatrix} \times \text{spins} \end{aligned}$$

$$D_6 \cdot D_6 = \delta_{\alpha''_j L''_j S''_j, \alpha'_j L'_j S'_j} \delta_{\mathcal{L}'_m \mathcal{L}'_j} \delta_{\mathcal{L}''_m \mathcal{L}''_j} \times \text{spins} \times \delta_{\alpha''_m L''_m S''_m, \alpha_m L_m S_m}$$
$$\delta_{\alpha''_m L''_m S''_m, \alpha'_m L'_m S'_m} (-1)^{\mathcal{L}'_m - \mathcal{L}_m} [\mathcal{L}''_i, \mathcal{L}_m]^{1/2} [\mathcal{L}''_i, \mathcal{L}'_m]^{1/2}$$
$$\times \left\{ \begin{array}{ccc} l_i & \mathcal{L}_i & \mathcal{L}''_i \\ L''_m & \mathcal{L}''_m & \mathcal{L}_m \end{array} \right\} \left\{ \begin{array}{ccc} l_i & \mathcal{L}_i & \mathcal{L}''_i \\ L''_m & \mathcal{L}''_m & \mathcal{L}'_m \end{array} \right\} \times \text{spins}. \qquad \text{(E.67)}$$

We obtain the following expression by summing over $\mathcal{L}''_i$,

$$\sum_{\mathcal{L}''_i} D_6 \cdot D_6 = \delta_{\alpha''_j L''_j S''_j, \alpha'_j L'_j S'_j} \delta_{\mathcal{L}'_m \mathcal{L}'_j} \delta_{\mathcal{L}''_m \mathcal{L}''_j} \times \text{spins}$$
$$\delta_{\alpha''_m L''_m S''_m, \alpha_m L_m S_m} \delta_{\alpha''_m L''_m S''_m, \alpha'_m L'_m S'_m} \delta_{\mathcal{L}_m \mathcal{L}'_m} \delta_{\mathcal{S}_m \mathcal{S}'_m}. \qquad \text{(E.68)}$$

Since subshells j and j' contain no more than one electron, the results for $D_7 \cdot D_7$ are the same as for Case 4, except that subshell $j-1$ is subshell$m$ as opposed to subshell i. However, $\mathcal{L}_m = \mathcal{L}'_m$ and $\mathcal{S}_m = \mathcal{S}'_m$, so we obtain the same solution as eq. E.60, so that we arrive at the following solution for $D \cdot D$,

$$\sum_{\mathcal{J}''} \sum_{\mathcal{L}''_q} \cdots \sum_{\mathcal{L}''_{j'}} D \cdot D = \frac{[\mathcal{J}_q]}{[l_j]} \delta\alpha\alpha'. \qquad \text{(E.69)}$$

For a multi-electron atom with no more than two electrons having the same principal quantum number, we arrive at a single solution,

$$\sum_{\alpha''} D \cdot D = \delta_{\alpha\alpha'} \sum_{config''} (n \cdot k) \frac{[\mathcal{J}]}{[l_\alpha]}, \qquad \text{(E.70)}$$

where l_α is the orbital angular momentum of the electron undergoing the transition while it is in state *alpha*. The sum over states α'' includes the sum over all total and intermediate angular momentum states, but in the process of reducing

our expressions, we either executed those sums or they were reduced to delta functions. As a result, we need only to sum over all possible the configurations of α'', remembering that the case when $alpha''$ is in the same configuration was addressed in section E.1.

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BIOGRAPHICAL SKETCH

Gwyneth Junkel-Vives was born April 18, 1965, in Oak Park, Illinois. She graduated from John Hersey High School, Arlington Heights, Illinois, in June 1983. She attended the University of Illinois, at Urbana-Champaign, where she received the degree of Bachelor of Science in engineering physics in May 1987. She also attended graduate school at the University of Illinois and received the degree of Master of Education in secondary education in January 1990. From September 1991, until June 1993, she taught physics and mathematics at Good Counsel High School, Chicago, Illinois. From August 1993, until the present she has been a graduate student in the Department of Physics at the University of Florida. She has accepted a post-doctoral position with the Atomic and Optical Physics group at Los Alamos National Laboratory, in Los Alamos, New Mexico.

Gwyneth Junkel-Vives is married to Dr. Thomas Edward Vives.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles Hooper, Jr., Chairman
Professor of Physics

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James Dufty
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Selman Hershfield
Associate Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

David Reitze
Associate Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James Winefordner
Graduate Research Professor
of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirments for the degree of Doctor of Philosophy.

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Dean, Graduate School